The CHEMICAL ACTION of ULTRAVIOLET RAYS

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THE CHEMICAL ACTION of ULTRAVIOLET RAYS

by

CARLETON ELLIS

and

ALFRED A. WELLS

Revised and Enlarged Edition

by

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BOOK DEPARTMENT

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Preface

The common need of workers in theoretical and industrial chemistry, biology and medicine for a modern reference work on photochemistry has led to the preparation of this revision of the familiar work of Ellis and Wells, *The Chemical Action of Ultraviolet Rays*. Recent theoretical advances have so altered the interpretation of many reactions as to require the rewriting of a large portion of the text. Incorporation of the results of the great recent activity in this field has necessitated considerable expansion. Certain explanatory chapters regarding the modern viewpoint have been added for readers who may not have had the advantage of recent advanced courses in physical chemistry. These chapters (1, 2, 12, 13, 14, 15 and 16) are intended to convey in non-mathematical fashion an understanding of the manner in which certain wave-lengths may supply the activation energies of chemical reactions.

The types of apparatus available for the production of ultraviolet rays are described in considerable detail in Part I. Particular attention is given to the influence of the operating conditions upon their outputs of energy. In dealing with photochemical reactions in Part II, a few representative reactions are at first discussed at length to illustrate the manner in which the mechanism of a reaction may be studied. Then, in subsequent chapters, the literature of a wide variety of photochemical processes is summarized. The effort has been made to include citations to all work subsequent to the first edition (1925), and in some instances references to the earlier work have been amplified. At many points it has been necessary to broaden the scope beyond the limitation implied by the title by including for comparison data on reactions due to visible light. In Part III, the effects of light on industrial products are treated in a somewhat more empirical manner, since as yet but few investigators in this field have made full use of the current theoretical advances. In reviewing the biological effects (Part IV), the emphasis has been placed upon the photochemical changes occurring in the compounds present in living cells and their resultant effects upon viability and function. A detailed historical account is given of the manner in which the combined efforts of physicists, organic chemists, biochemists and medical investigators have advanced our knowledge of the action of ultraviolet radiations in the formation of the D vitamins. The engineering and public health aspects of this work have not been neglected. The scope and limitations of irradiation therapy in conditions other than rickets have been considered, but the details of treatment have been left for medical monographs. Recent applications of ultraviolet energy in the sterilization of various materials are mentioned.

Absorption spectra, fluorescence, photoelectric effects and other physical topics are described only insofar as they contribute to an understanding of the mechanism of photochemical reactions. Such purely physical applications as spectrographic analysis and fluorescence tests of materials are discussed only to an extent sufficient to make clear their relation to other more pertinent topics, although sources of information regarding them are given.

It is a pleasure to acknowledge the courtesy of the Hanovia Co. and the General Electric Vapor Lamp Co. in supplying unpublished data regarding newer forms

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of mercury discharge tubes. The Atlas Electric Devices Co. and the National Carbon Co. have furnished numerous illustrations. Many authors and publishers of books and journals, too numerous to mention, have permitted the publication of illustrations from their work. Drs. D. A. Wells, W. M. Burgess and the late Albert Sherman have read certain chapters and offered valuable suggestions. The authors of the first edition have been especially helpful. Many reference books, review articles and incidental summaries, as well as abstracts of patents and of material in difficultly accessible sources, have been freely used. The effort has been made to acknowledge these in suitable places.

FRANCIS F. HEYROTH.

Institute of Scientific Research
University of Cincinnati
June, 1940

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Chapter 1

Introduction: Nature of Ultraviolet Radiation

The agency of light and the field of photochemistry, aside from photography, have until recently received relatively little use on a commercial scale. To be sure, a few photochemical processes of an industrial character, such as the production of benzyl chloride, have had a limited commercial application, but most chemical operations utilizing the agency of sunlight have been found slow and ineffective. In contrast with the industrial applications, theoretical photochemistry has recently attracted many workers, and a few guiding principles, together with a considerable amount of detailed information, have been obtained during the past three decades. Much of this advance has been due to the study of the effects of ultraviolet radiation which, following the development of suitable sources, has been carried on with vigor.

Everyone is familiar with the application of ultraviolet irradiation methods to the problem of enriching the vitamin D content of milk and of certain other foodstuffs and pharmaceutical products. The number of branches of chemistry in which this radiation has been studied is, however, often a source of surprise to chemists when they first become cognizant of the facts. This is largely because comparatively few industrial operations are carried out with this form of radiant energy.

Foodstuffs, the fuels which supply the energy of all animal life, are built up by the action of sunlight in plants. Desirable as it might be to develop ways of replacing the present farming methods by well-controlled photochemical operations conducted in a factory, this is of less immediate importance than the problem of the exhaustion of natural fuels which serve as sources of energy for our mechanized civilization. Coal and oil represent the stored vegetation of the past. In an address on the future problems of engineering, Parsons[1] pointed out the limitations imposed by thermodynamics upon the utilization of fuels and emphasized the imminent need for studies of the availability of other sources of energy. After considering hydroelectric power sources and the other less explored possible sources of energy such as the atom, the heat of the earth, tides, waves and wind, he concluded that the most promising source is the sun. For the utilization of solar energy it may be necessary to find reactions which will yield compounds of high energy content which can serve as storage reservoirs.

Magnitude of Solar Energy

From the time of Joseph Henry, workers at the Smithsonian Institution, including particularly S. P. Langley and, at present, Charles Abbot, have made many measurements of the total amount of energy received on the earth from the sun at a number of stations throughout the world. The solar constant is defined as the solar energy which impinges in unit time on unit area of a surface perpendicular to a sunbeam just outside the earth's atmosphere. Observations made at the

[1] Parsons, W. B., *J. Frank. Inst.*, **200**, 219 (1925).

earth's surface are corrected for the loss of about 30 per cent which occurs during the passage of the light through the atmosphere. The mean value of the solar constant has been found to be 1.94 calories per minute per square centimeter, equivalent to 1.35×10^6 ergs per square centimeter per second. The fluctuations of 2 to 3 per cent on both sides of the mean appear to be associated with the eleven-year sunspot cycles, the radiation being greatest when the spots are most numerous.

Stewart [2] has made calculations which enable one to visualize the meaning of these figures in comparison with the amounts of energy available from other sources. He concludes that the sun at the zenith supplies the outer atmosphere with 4,690,000 horsepower per square mile. At the surface this is equivalent to about $4{,}690{,}000 \cos\theta \times (0.70)^{\sec\theta}$ where θ is the angle between the sun and the zenith. The maximum power output of Niagara Falls is estimated at about 4,000,000 H.P. At noon on a clear day in June, the sunlight falling on 133 square miles at Philadelphia is equivalent in power to 100 Niagaras; it is about 70 per cent less in December. If the radiation which strikes the whole earth in a single second could be converted into power, its value, at one cent per kilowatt-hour, would be nearly half a billion dollars. Parsons stated that, assuming the total span of daily sunlight to be equal to nine hours of maximum intensity and 50 per cent of the energy to be recoverable, a strip of land 10 miles wide and 100 miles long would develop daily as much power as could have been obtained from one-half the world's total fuel consumption in 1920, allowing three pounds of coal per horsepower. The area of Salt Lake, Utah, alone would suffice to produce energy equal to that furnished by the whole annual world consumption of coal.

As the earth intercepts only one part in 22,000 millions of the total energy radiated by the sun, it may be calculated that the sun emits nearly 75,000 H.P. per square yard of its surface. At one cent per kilowatt-hour, its power output would be valued at "a billion dollars in a billionth of a second."

Attempts made thus far to utilize this energy have been limited to the use of aqueous vapor as an intermediary in an engine operated by very low steam pressure. According to Parsons, the maximum overall efficiency obtained in the Shuman-Boys absorber in Meadi, Egypt, was 4.32 per cent. As yet few, if any, attempts have been made to concentrate the sun's rays by a system of reflectors upon chemicals in order to get the latter to react to produce others of high energy content and fuel value.

The conscious development of such ideas has instead been concentrated largely upon the problem of the mechanism by which chlorophyll enables plants to utilize solar energy in building up the compounds which serve as foods.

Nature of Radiant Energy

An understanding of the chemical reactions produced by ultraviolet radiations requires a knowledge of their physical nature. As they represent but one of the forms of radiant energy which comprise what is called the electromagnetic spectrum, there is given in the following portions of this chapter a brief historical sketch of the present knowledge of light, visible and invisible. There is an essential physical unity in the nature of wireless waves, infrared radiation, visible light, ultraviolet radiation, x-rays and gamma-rays. Photochemical changes induced by visible light and by ultraviolet radiations are quite similar in mechanism, differing chiefly in the amounts of energy involved and in the types of equipment necessary.

[2] Stewart, J. Q., *J. Frank. Inst.*, 204, 438 (1927).

These two forms of radiant energy are distinguished by special names merely because our eyes permit us to appreciate the presence of the visible but not of the ultraviolet radiations.

Since 1913 conceptions derived from the study of the mechanism of the production, transmission and absorption of radiations have come to dominate and transform modern chemistry and physics. They have been applied with great success to the problem of the constitution of the atom, affording models by which to express the facts embodied in the periodic table. Very recently, they have led to new methods of studying the nature and strength of the chemical bond and have given rise to a new attack on the fundamental problem of chemical affinity.

Each of the forms of radiant energy is transmitted through a vacuum at the same rate, 186,000 miles per second or 3×10^{10} centimeters per second, the long-known velocity of light. The manner in which light is transmitted through space has been for more than two centuries the subject of a controversy between the adherents of the wave and corpuscular theories, the origin of neither of which is certain.[3]

The inadequacy of a corpuscular theory to account for the phenomena of diffraction and interference led Huyghens in 1690 to state, without claiming the idea as his own, that light is made up of waves which he conceived as longitudinal pulses extending in all directions from a center of disturbance along a spherical front. He did not, however, conceive of the existence of a train of waves. Newton, the discoverer of the resolution of white light into a spectrum by means of a prism, on the other hand, favored the view that light is transmitted as minute corpuscles ejected through space, since he believed (1672) that a wave theory could not account for the rectilinear propagation of light. He described the phenomena of diffraction of light passing between closely spaced knife edges and the famous rings of color observed in thin plates, now known to be due to interference. Both of these phenomena now, as then, afford the strongest evidence for the wave nature of light. Newton [4] ascribed them to certain "fits" of reflection or transmission. Notwithstanding the fact that Huyghens had shown it possible to explain the rectilinear propagation of light and the phenomena of refraction by certain geometrical constructions regarding the advancing wave form, confusion reigned for about a century.

By extending the wave theory to include a continuous series of periodic waves, Dr. Thomas Young was able to explain the phenomenon of interference and to demonstrate it in a famous experiment in a Bakerian Lecture before the Royal Society in 1801. Light from a single source was made to pass through two very closely adjacent pinholes and illuminate a spot upon a screen. At the spot where the two cones of light overlapped, dark and light bands are observed. Any point within this area receives light by two different paths, one from each pinhole. If the lengths of these paths differ, the crest of a wave reaching it by one path may meet the trough of a wave reaching it by the other; with a different ratio of the lengths of the paths, a spot nearby may receive the crests of both waves. In the former case the crest and trough (then believed to be points of maximum compression and rarefaction) annul each other, are said to interfere, and the spot receives no illumination. In the latter case the waves add together and the spot is very bright.

This experiment regarding the nature of interference turned the tide in favor of the wave theory of light. In the early theory, the waves were conceived as

[3] Crew, H., *J. Opt. Soc. Am.*, 20, 6 (1930).
[4] Newton, Sir Isaac, "Optics," 1704.

longitudinal compressions and rarefactions of the ether similar to those by which sound is transmitted by air. New difficulties were introduced by the discovery of the phenomenon of the polarization of light (Malus, 1809) and the investigation by Arago of the rotation of the plane of polarization by various substances. These phenomena, unlike any encountered in the case of sound, eluded explanation until Fresnel in 1821 published the brilliant suggestion that the light waves may be vibrations transverse to the direction of propagation of the spherical wave-front.

Wave-length and Its Measurement

1. Fundamental Concepts and Methods. The distance from crest to crest or trough to trough of a series of waves is known as the wave-length. For visible light it is very small and must be measured in suitable small units. That the wave-length has for each color a constant and characteristic value was indicated by later interference experiments of Young.

While all colors of light travel at the same rate in a vacuum, this is not the case when they pass through transparent material bodies. In going from a light medium to a denser one the velocity of light is slowed to an extent which depends upon the wave-length. For this reason, white light in passing through a prism is spread out into a spectrum of colors. The greater the thickness of the path of light in the prism the greater the resolution or spreading of the spectral colors. Measurements of the wave-length of light in some limited spectral regions, as for example the yellow, were early made by means of an experimental arrangement based upon the interference of waves reaching a spot along paths of slightly different lengths.

For precise measurements of this sort the particular region at which the measurement is made must be reproducibly defined. Fraunhofer found in the solar spectrum a series of dark lines which serve as natural landmarks for certain wave-lengths, rendering the location of a given point in the spectrum possible irrespective of the resolution of the prism. It was later found that these lines correspond in wave-length to the bright lines found to be superposed on a continuous colored background when certain elements are heated to high temperatures. Kirchhoff found that the elements which emit these lines are also capable of absorbing them when the vapors of the elements are placed between a continuous source and the spectrograph. The theory of the origin of the Fraunhofer lines in the solar spectrum is that certain elements in the gaseous atmosphere of the sun absorb the sun's radiations at just these wave-lengths, and so lessen their brilliance in the solar spectrum.

In 1823 Fraunhofer made precise measurements of the wave-lengths of the chief dark lines which occur in the solar spectrum. He employed for this an instrument based upon the principle of interference, the optical grating. With a diamond, he ruled a great number of equally and very closely spaced parallel lines in a thin film of gold deposited on a glass plate. This grating simulates a prism in its ability to separate the wave-lengths of light; unlike the prism it permits the wave-length of any line to be measured by direct methods described in detail in any textbook on optics.

Because of the likelihood of mechanical imperfections in the ruling of even the best gratings (such as those ruled by Rowland) Michelson, in 1893, turned to the use of interferential apparatus. This represents a simplification of the principle of the diffraction grating, since the many thousands of waves which act simultaneously in grating experiments are, in the interferometer, replaced by but two with a very large difference in path. The interferometer offers resolution practically without limit. Its use showed that spectral lines are often accompanied by other lines called "satellites" and made possible the development of modern theories of the multiplicity of spectral lines.

With the help of Benoit in the Bureau Internationale des Poids et Mésures, Michelson determined the wave-length of the cadmium red line with a precision far beyond that of all previous workers. By the use of a new interferometer, Fabry in 1900 and Perot [5] compared the wave-length of the red cadmium line with the standard meter in Paris and found the wave-length to be equal to 0.00064384696 mm., the observations being taken in dry air at 18°C. and at a mercury pressure of 76 cm. This value agreed well with that of Michelson who reported 0.00064384700 mm. for the same line. Seven years later Fabry and Buisson investigated certain other wave-lengths and from these measurements there developed the international system of wave-lengths, the precision of which is probably one part in a million in absolute as well as in relative values. Standard values for many lines can be found in the "International Tables of Critical Constants." It may at first seem that such precision is unnecessary. Recently, however, numerical relations have been discovered between the wave-lengths of different spectral lines emitted by the same element and these have led to the development of theories of atomic structure. At the present time the details of the structures of individual lines are being actively investigated. This work requires data of high precision.

2. Units. The minuteness of the wave-lengths of the colors of visible light makes it desirable to express them in terms of units of length much smaller than the millimeter. In the ultraviolet, and sometimes also in the visible range, the Ångström unit is employed. This is defined as 1×10^{-8} cm. It is commonly abbreviated by the letter A rather than the Swedish Å. The cadmium red line is 6438.4696A. In the visible region many workers employ a unit, ten times as large as the Ångström (10A), called the millimicron. A micron is the millionth part of a meter and the millimicron is the thousandth part of this, since *milli* in the metric system means "the thousandth part of" the unit to which the term is prefixed. It is correctly designated by the symbol mμ, since the letter "m" is the standard abbreviation for milli, and μ that for the micron or, in general, "millionth part of." [6]

Another manner of designating or identifying a given radiation is based upon the velocity with which light travels in a vacuum. The number of wave crests which pass a given point in a second, *i.e.*, the frequency of the light, is obtained by dividing the velocity of light expressed in centimeters per second by the wave-length in question expressed in centimeters. Frequencies are of importance in connection with modern views of the mechanism of the emission of light from hot bodies. They involve very large and unwieldy numbers.

Smaller figures may be obtained by dividing the true frequencies by the velocity of light. The units so obtained are known as wave-numbers and represent the number of crests within a distance of one centimeter of a wave-train viewed instantaneously. The wave-number is obviously the reciprocal of the wave-length expressed in centimeters, rather than in Ångström units. It has been much employed in recording the data of spectroscopy.

[5] This account has been derived largely from an address by Charles Fabry, The Franklin Institute Centenary Lecture, Sept. 17, 1924.

[6] Following Kayser, the German authority on spectroscopy, the millimicron has been abbreviated as $\mu\mu$ by many writers. This is erroneous since it would logically mean the millionth part of the millionth part of a meter. The error was pointed out by Guillaume, director of the International Bureau of Weights and Measures in 1913, but the misleading symbol is still frequently encountered. Camp, J. P., *Science,* **70,** 453 (1929); Dorsey, N. E., *Ibid.,* **71,** 67 (1930).

Invisible Radiations

The visible spectrum covers only the short range of wave-lengths from 7200-7600A at the red end to 3900-4000A at the violet end, the exact limits varying from one person to another, and from one species of animals to another. In 1800, Sir William Herschel discovered that the heating effect of sunlight was not confined to the visible portion of the spectrum from a prism since a thermometer placed beyond the red end where nothing could be seen showed a higher temperature than when exposed to the red rays. About this time the existence of some form of energy beyond the violet end of the spectrum was demonstrated independently by Ritter and by Wollaston (1802). They showed that the decomposition of silver chloride (which occurs in the visible range as shown by Scheele in 1777) proceeded even more rapidly in the invisible region.

It was soon noted that both the heating effects of the infrared region and the chemical activity of the ultraviolet region are due to radiations of the same general nature as those producing visible light. Thomas Young showed the energy in the ultraviolet to be of wave nature by obtaining records on silver chloride paper of interference rings produced in this region. Phenomena of diffraction and interference were demonstrated in the infrared by Fizeau and Foucault in 1847. The occurrence of Fraunhofer lines in the infrared region of the sun's spectrum was demonstrated by Herschel in 1840; Becquerel photographed them in the ultraviolet region.

In 1860, James Clerk Maxwell laid the foundations of the modern theory of all these radiations by relating the mathematical theories of Green, Stokes and Kelvin, for wave motion as a generalized process, to the experimental demonstrations by Faraday of the electromagnetic fields set up by the motion of electric charges. He showed on theoretical grounds that electromagnetic waves should travel with the velocity of light and indicated that all these forms of radiant energy consist of such waves.

Fitzgerald showed in 1883 that a coil carrying a rapidly alternating current should radiate waves into the surrounding space. About 1886, Hertz produced these waves by means of an oscillatory discharge across a gap. He also developed methods for detecting and measuring the wave-lengths of these electromagnetic waves, which can be greatly varied, and showed that they can be reflected and refracted like light. Within a few years, Marconi employed them in wireless signaling.

Radio waves are millions or billions of times longer in wave-length than are those of visible light. The waves produced by Hertz were much shorter in wave-length than those employed in radio transmission. Recently, by a refinement of the method employed by Hertz it has been possible to obtain waves having lengths of only 0.1 to 0.2 mm.[7] These are shorter than the longest infrared rays from the mercury-vapor lamp (0.4 mm.) or the Welsbach burner (0.6 mm.) as measured by Rubens. The wave-length regions of the Hertzian and infrared waves thus overlap and there is no fundamental distinction between these forms of radiant energy. The only reason for applying different names is to emphasize the experimental techniques employed for their production.

Radiations Beyond the Violet

In studying the ultraviolet region the same methods of resolution employed in the visible, the prism or the diffraction grating, have been used. For detection

[7] Nichols, E. F., and Tear, J. D., *Proc. Nat. Acad. Sci.*, **9**, 211 (1923).

of the radiant energy, a photographic plate usually serves. If one passes progressively toward the short wave-lengths, the study of the ultraviolet begins with a minimum of difficulty. But as one advances into the shorter wave-lengths the difficulties increase. At about wave-length 3400A, glass becomes so strongly absorbing that it is no longer of service and must be replaced by quartz or some similar crystalline substance. At about 2900A, the solar spectrum ends, due to absorption by ozone in the higher levels of the earth's atmosphere. By the use of artificial sources, such as the metallic arc, the short wave-lengths may be supplied in satisfactory intensity. It is comparatively easy to photograph and measure wave-lengths as short as 1850A, this limit having been reached by Cornu. From this point the difficulties increase very greatly as quartz becomes strongly absorbing and the gelatin of the photographic plates becomes so opaque that the radiation does not penetrate it and so can no longer act upon the silver salt. Finally, with still shorter waves, air itself ceases to be transparent, all radiations being absorbed in a very small thickness. Schumann, working between 1890 and 1903, overcame these difficulties by replacing the quartz by fluorite, by placing the apparatus in a vacuum and by making photographic plates with emulsions containing a minimum of gelatin.[8] By the methods of Schumann it was possible to obtain the spectrum of hydrogen to 1200A, at which point fluorite ceases to be transparent. Schneider[9] has suggested that lithium fluoride may be employed in place of fluorite.

Schumann did not actually measure the wave-lengths but only estimated them by means of an extrapolation of the dispersion formula for fluorite. Particularly active among more recent workers in the Schumann region have been Leon and Eugene Bloch[10] who studied many lines of manganese, chromium, silver, gold and platinum sparks of wave-length between 1869 and 1330A.

For working further into the ultraviolet, the concave grating is employed as the resolving medium; as in the visible range, it has the advantage of giving directly the lengths of the waves. The grating, usually of about one meter radius, is placed[11] in a container maintained at a very high vacuum. As, however, the gas pressure surrounding the spark which serves as the source of light cannot be too low, matters must be so arranged that the gas surrounding and carrying the discharge is not allowed to enter into the body of the spectrograph. This is done by separating the source from the rest of the apparatus by a short and narrow slit and applying a powerful mercury diffusion pump at a point just beyond this slit. With this arrangement, Lyman succeeded in determining the lengths of the waves studied by Schumann; in addition to this, he extended the optical spectra to 510A in the case of helium.

Millikan, Bowen and collaborators, as well as Edlén[12] and others, have subsequently measured lines (emitted by hot sparks) as short as 40.28A in the case of the stripped carbon atom. The existence of much shorter radiations than these had, however, been known since the discovery of x-rays by Röntgen in 1895 and of gamma-rays by Villard in 1900. X-rays have wave-lengths of the order of molecular dimensions or less. Laue, in 1912, conceived the idea that the natural strata of a crystal might serve as a diffraction grating for such short wave-lengths, since the distance between the rulings would be that separating the rows of atoms

[8] Directions for making these plates are given by Hopfield, J. J., and Appleyard, E. T. S., *J. Opt. Soc. Am.*, **22**, 488 (1932).

[9] Schneider, E. G., *J. Opt. Soc. Am.*, **27**, 72 (1937).

[10] Bloch, L. and E., *J. Phys. Radium*, **6**, 154 (1925).

[11] Lyman, T., *J. Frank. Inst.*, **201**, 556 (1926); *Astrophys. J.*, **60**, 1 (1924); Wood, R. W., and Lyman, T., *Phil. Mag.*, **2**, 310 (1926).

[12] Edlén, B., *Nature*, **127**, 405 (1931).

in the crystal. On sending a bundle of x-rays through a suitable crystal the expected phenomenon of diffraction appeared. A short time later, Bragg attacked the problem by studying the reflection from a crystal face and succeeded in measuring x-ray wave-lengths.

The characteristic x-rays of the elements range from 22A for the K-absorption edge of uranium to 0.107A. The longest x-rays measured by the Bragg crystal diffraction method are 21.53A, for one of the lines of chromium.[13] Compton[14] and also Thibaut[15] have shown that ruled gratings of the kind used for measuring the wave-lengths of ordinary light can be employed to demonstrate the diffraction of x-rays striking the grating at very small grazing incidence. This method has been much employed in studying the region between the x-rays and the shortest ultraviolet rays.

Recent absorption measurements in the Schumann region show that many common compounds absorb these ultraviolet rays and suffer decomposition thereby. The photochemistry of this region seems destined to provide many important observations.

The physicist has made considerable progress in exploring the region of wave-lengths somewhat longer than the usual x-rays by estimating the wave-lengths by the indirect method of resonance potentials. The usual method of x-ray generation is by the bombardment of a metal target with high-speed cathode rays. A modification permits the generation of radiations within the longer wave-length range. The substance which is to emit the rays is bombarded by a stream of thermionically-produced electrons moving at lower velocities produced by accelerating them by definite alterable electrical potential differences. The energy which the bombarding electrons can give to the atoms bombarded is thus known and may be expressed as the product of the charge of the electron and the potential gradient in volts per centimeter. The energy is in this way stated in units called electron-volts. Since the charge on the electron is constant, the energy is sometimes expressed less accurately as volts, for brevity. As the acceleration of the electrons is gradually increased by raising the potential difference between a plate and a charged grid through which the electrons pass, the energy possessed by the electrons becomes great enough to enable them, on striking atoms in the gaseous space through which they pass, to excite the atoms to emit radiation. Certain critical energies (in electron-volts) are necessary for this to occur. The critical voltages are obtained in such experiments by finding certain discontinuities in the current carried by the electron stream as the charge on the grid is progressively changed. At 4.9 volts, in the case of mercury vapor as the emitting atom, a single line with a wave-length of 2537A appears. This is called the mercury resonance line. At 6.7 volts, one with a wave-length of 1844A flashes out. The frequencies corresponding to the emitted wave-lengths are calculated by dividing the energy by a fundamental constant of nature, the quantum of action or Planck's constant, the nature of which will be discussed in the next chapter.

The method has been extended to the region of wave-lengths only slightly longer than x-rays. The emission of radiations in such experiments is made evident by a sudden increase of gaseous ionization or of photoelectric effect as the accelerating voltages are gradually raised beyond the critical values. Holweck[16]

[13] Thoraeus, R., *Phil. Mag.*, **1**, 312 (1926).

[14] Compton, A. H., *Proc. Nat. Acad. Sci.*, **11**, 598 (1925).

[15] Thibaut, J., *Compt. rend.*, **182**, 55, 1141 (1926); **185**, 62 (1927); *J. Phys. Radium*, **8**, 13 (1927); *Nature*, **121**, 321 (1928); *Physik. Z.*, **29**, 241 (1928); *J. Opt. Soc. Am.*, **17**, 145 (1928); De Broglie, *Compt. rend.*, **190**, 93 (1930).

[16] Holweck, F., *Compt. rend.*, **173**, 709 (1921); *J. Chim. Phys.*, **22**, 311 (1925).

has shown that a continuous radiation is produced when accelerating voltages between 25 volts (500A) and 280 volts (44A) are employed. He used an apparatus consisting of a sort of Coolidge x-ray tube made entirely of metal in which the cathode and anode are separated by a distance of one millimeter. The tube is operated at potentials of 25 to 1800 volts. As the rays emerge from the tube through celluloid films of a thickness of 0.00005 mm., they enter an ionization chamber. Superposed on the continuous spectrum there is a line spectrum characteristic of the element used as a target.

These radiations lack penetrating power; this is the reason why it is necessary to use the thin celluloid window. They are said to be soft x-rays. The term hardness connotes penetrating power. Soft x-rays (but not as soft as those of Holweck) have been used by Günther[17] in the examination of thin layers of biological products such as leaves or the wings of insects. These rays, which because of their greater ease of absorption, are better suited than hard x-rays for the treatment of skin diseases, are produced in tubes operated at voltages low (4 to 12 kilovolts) compared with those used for more penetrating x-rays. Egress is through a window of a special glass in which sodium, calcium and silicon have been replaced by lithium, beryllium and boron.

As the wave-lengths increase from the x-ray to the ultraviolet region, the absorption of the radiations by many substances increases to a maximum beyond which there is a diminution in absorption as the better-known regions of the ultraviolet are reached. Holweck found that 0.00027 mm. of celluloid, which has a relatively low absorption in comparison with other substances in this region, transmits only 3 per cent of the radiation of wave-length 310A at which it has its maximum absorption.

The gamma-rays produced by radioactive decay, as measured by Ellis, have wave-lengths between 0.26 and 0.005A. Very penetrating radiations known as cosmic rays, discovered by Wulf and by Gockel between 1909 and 1914[18] have recently been the subject of particularly extensive investigation by Kolhörster, Regener, Millikan, Compton, and many others. Although some workers consider them as electromagnetic waves of extremely high frequency, most believe them to be some type of high velocity movement of minute corpuscles. They are certainly non-homogeneous; the highest frequency band has so enormous a penetrating power that it passes through 200 feet of water or 18 feet of lead before being completely absorbed, although two or three inches of lead absorb the hardest gamma-rays.

The Electromagnetic Spectrum as a Whole

The radiations from wireless telegraph waves to gamma-rays which make up the electromagnetic spectrum are summarized graphically in Figure 1. The range of wave-lengths is so great that a logarithmic scale is required. A doubling of the wave-length is called an octave, a familiar term in music. The diagram of the electromagnetic radiations covers about sixty octaves, and of these, only one represents the radiations which are visible. In certain regions, as between the Hertzian and the infrared regions, an overlapping of the radiation known by various names, is indicated. This means merely that radiations of wave-lengths included in the region of overlapping have been produced by the methods which are usually employed for the production of wave-lengths on both sides of this

[17] Günther, P., *Z. Angew. Chem.*, **44**, 404 (1931).

[18] Compton, A. H., *Nature*, **135**, 695 (1935). The existence of a shortest possible wave-length of 6.2×10^{-5}A has been assumed by A. March, *Z. Physik*, **108**, 128 (1937).

region. A consideration of the mechanisms by which radiations are produced indicates that the nature of the oscillator bearing the charge, whether it be a coil of wire, a molecule moving as a whole, valence electrons in a molecule or atom, or nuclear electrons, usually determines, although in a very indirect manner, the wave-length of the radiations produced.

It is the wave-length which serves to characterize the nature of a radiation and to indicate its penetrability, chemical and optical properties and utility. The amplitude of the wave (or more accurately, the square of the amplitude) serves to visualize the intensity of the radiation.

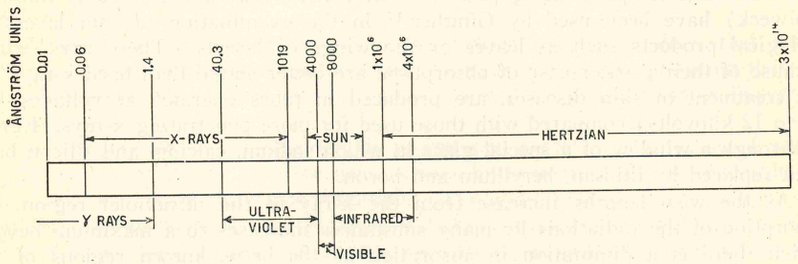


FIGURE 1. Electromagnetic Spectrum.

The impression has been given in the preceding discussion that the wave theory offers an adequate expression of the behavior of radiant energy. It must now be pointed out that there are a considerable number of effects, particularly those concerned with the mechanism of the emission and absorption of radiant energy, for which the wave theory has no ready explanation. These effects are better comprehended on the basis of the quantum theory, according to which quanta or "bundles of energy" are emitted from the source, as explained in the following chapter. The quantum theory may be adequately applied over a considerable field, notably to photoelectric phenomena, Bohr's theory of the atom, and the relationship between the frequencies of lines in emission spectra. Indeed, it has served in the last few years as a great correlating principle for a wide variety of physical properties as diverse as the specific heats of elements and the absorption of radiations.

Great changes in physical theory have arisen from the recent work of De Broglie, Schrödinger and of Heisenberg. Their theories have led to the creation of a new system of mechanics in which the motion of a material particle is always associated with a wave motion, the wave-length of which is determined by dividing Planck's universal constant by the momentum of the moving particle. Conversely, in the words of Planck, radiant energy traveling with the speed of light appears on interacting with matter, to "shrink together and concentrate itself at separate points which move like corpuscles, and for that reason are called light-quanta." [19] Each such quantum of radiation is now called a *photon*.

It appears from the newly established points of view that there can be neither pure corpuscular motion nor pure wave motion in physics. Rather, every corpuscular motion is attended by some measure of wave motion and every wave motion involves something of corpuscular motion. The distinction between the

[19] Planck, M., *J. Frank. Inst.*, May 18, July 15, 1927.

two is only gradual and quantitative. The acceptance of such an unlooked-for conception has followed from the experiments of Davisson and Germer [20] which, by revealing the diffraction of electrons, demonstrated the motion of even these minute particles to be such as to imply a wave-nature for them.

On the other hand, the elementary quantum plays no part in the equations of Maxwell for radiant energy, which have not been invalidated in even the finest interference measurements. At present, therefore, physicists and photochemists employ both the wave and the quantum aspects of radiant energy in interpreting their data. Wave-lengths or frequencies are used to designate the quality of a radiation, but in discussing its photochemical effects quantum concepts are necessary.

[20] Davisson, C., and Germer, L. H., *Phys. Rev.*, **30**, 705 (1927); Thomson, G. P., *Proc. Roy. Soc.*, **A117**, 600 (1928).

Part I

The Sources of Ultraviolet Radiations

Chapter 2

Mechanism of the Emission of Radiant Energy

The occurrence of a photochemical reaction in the ultraviolet region presupposes the absorption of ultraviolet radiation. An understanding of the mechanism of the reaction involves a knowledge of the processes by which the radiant energy is absorbed by one or more of the reacting substances. Since the time of Kirchhoff it has been realized that absorption of radiant energy is the converse of the process by which it is emitted. Reference to this has been made in the preceding chapter in the discussion of the well-known Fraunhofer dark lines in the spectrum of the sun. Since our present views regarding the interaction of radiant energy and matter were derived chiefly from studies of the manner in which matter emits radiations, it seems logical to describe the emission mechanism of the ultraviolet sources in common use before proceeding to a consideration of the absorption of radiations by substances concerned in chemical reactions.

Illuminating sources consist of some form of matter heated to incandescence, such as the carbon particles in an oil lamp or the luminous flame of a gas burner, glowing calcium oxide in the old limelight, rare-earth oxides in the Welsbach gas mantle, or electrically heated wires glowing in an atmosphere of inert gas. When, as in the first of these, the temperature is relatively low, the color of the rays emitted is a mixture of red and yellow. Sources at higher temperatures emit increasing quantities of blue rays so that the color of the light appears more nearly white. At still higher temperatures increasing amounts of the shorter ultraviolet rays appear.

In 1869, Stefan showed that the total amount of energy emitted by a black body increases as the fourth power of its temperature. Although the term "black body" refers to an idealized concept like that of a perfect gas, Stefan's law applies as an approximation to many substances. In experimental work, it may be approximated by a hollow sphere raised to a suitable temperature. The radiation emerging from a small hole is dispersed by a prism or grating and the intensities of the radiations in the various spectral regions are measured by a thermopile and galvanometer. Data of this sort are shown by the curves of Figure 2 in which the abscissae represent wave-lengths and the ordinates intensities in arbitrary units. Curves for three temperatures are included. They rise with increasing temperature in accordance with the Stefan-Boltzmann law; the areas beneath the curves vary as the fourth power of the temperature.

It may also be noted that as the temperature is increased, the wave-length of the maximum intensity shifts from the infrared region to the visible range. The red just begins to show at a temperature of approximately 1500°Abs. and the maximum lies at approximately 20000A. At the temperature of the tungsten lamp (2000°Abs.), the maximum is at 15000A. At solar temperatures (approximately 6000°Abs.), it is in the green region, a considerable proportion of ultraviolet rays also being emitted. Wien's displacement law states that with rising temperature the emission shifts to higher frequencies.

After the establishment of these two laws of radiation, physicists sought a theoretical explanation of the manner in which an increase in the temperature of a substance might cause it to emit electromagnetic waves. Since such waves in the Hertzian region are known to be produced by the oscillation of an electrical charge, it appeared necessary to conceive of some type of charged oscillator either borne

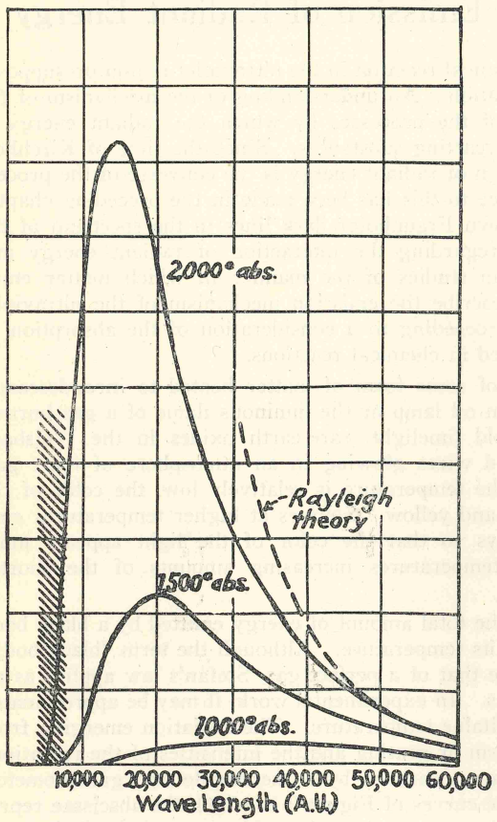


FIGURE 2.

Influence of Temperature on Blackbody Radiation (Eldridge, "Physical Basis of Things," New York, McGraw-Hill Book Co.).

by or located within the atoms of the solid which emits radiations. Mathematical physicists, notably Lord Rayleigh, Maxwell, and Jeans, attempted to develop a theory for the distribution of energy emitted by various hypothetical oscillators, with frequencies dependent upon the temperature. However, these attempts all led to the conclusion that when radiant energy is in equilibrium with matter, the total amount of radiant energy per unit volume should be infinite and that most of it should lie in the short-wave region of the spectrum. Actually, the laws of Stefan and Wien show that but a finite amount of radiant energy can be in equilibrium with matter at a given temperature, and that only at high temperatures does much of it lie within the ultraviolet.

This impasse was overcome by Planck,[1] who in 1900, advanced a theory of radiation in which the motion of hypothetical oscillators could be made to account for the radiation of energy in the amounts and wave-length distribution required by the laws of Stefan and Wien. Its acceptance was delayed because, in his derivation, Planck had been obliged to make certain assumptions at variance with the dynamics based upon Newton's laws of motion. The assumption was made that the energy of a vibrator in the heated body is increased only by jumps as the temperature is increased. These discontinuous increments of energy were called quanta and led to the name of quantum theory for the new viewpoint.

The investigations of Einstein[2] on the photoelectric effect did much to secure acceptance for the quantum theory, since they demonstrated the existence of discontinuities in the interaction of matter and radiant energy. Additional justification for the adoption of the radical concept of a discontinuity in the energies associated with matter in motion came in 1912 from a field of physics at first sight far from that of radiation when Debye[3] successfully applied the quantum theory to the study of the specific heat of solids. Perhaps the greatest factor which contributed to the present general acceptance of the quantum theory was the success of the work of Bohr on the interpretation of spectra, which was founded upon that theory.

It is the purpose of this chapter to acquaint the chemist who may be untrained in modern physics with that minimum of the newer viewpoint necessary for an understanding of the characteristics of the useful sources of ultraviolet radiations.

To that end, it is necessary first to inquire into the meaning of Planck's assumption. His idea implies that a physical system can exist in only certain discrete energy states. On the acquisition of energy, a system jumps from one to another of these states without passing through a continuous series of intermediate ones. A rotating dumbbell possessing a definite angular momentum can acquire energy and assume a new state of more rapid rotation with greater angular momentum. It is usual to think of it doing so by speeding up through all intermediate speeds of rotation. The quantum theory, however, makes the radical assumption that this is not the case and that, in speeding up, the change in rotational energy is discontinuous. Only certain rotational energies can be possessed by the dumbbell, and when speeding up, it can jump only from one to another of these. At first sight this seems contrary to everyday observation. This is not, however, necessarily the case because the energies possessed by a large object in the permissible states differ so little that the speeding-up process appears to be continuous. Matters are quite different in the case of minute systems such as those of atoms or electrons where the discontinuity of the process dominates the picture. Poincaré has shown mathematically that the fact that the total radiation from a black body at a finite temperature is finite requires that the ultimate motion involved in the mechanism of radiation be in some way discontinuous.

Since the work of Planck, different, and in some respects more satisfactory, derivations of the quantum laws of radiations have been given by Jeans,[4] by Darwin and Fowler,[5] and by Einstein.[6] The last of these, which has led to one of the fundamental laws of photochemistry, requires that the molecules emitting

[1] Planck, M., *Ann. Physik.*, **4**, 553 (1901).
[2] Einstein, A., *Ann. Physik.*, **20**, 199 (1906).
[3] Debye, P., *Ann. Physik.*, **39**, 789 (1912).
[4] Jeans, Sir J., *Phil. Mag.*, **20**, 953 (1919).
[5] Darwin, C. G., and Fowler, R. H., *Phil. Mag.*, **44**, 450 (1922).
[6] Einstein, A., *Physik. Z.*, **18**, 121 (1917).

radiations can exist only in certain definite energy states, and that when a molecule jumps from one state to another the accompanying loss or gain of energy is always one or more complete quanta of radiation, fractions of a photon not being emitted or absorbed.

It is as meaningless to speak of the amount of energy in a quantum without specifying its frequency as it would be for a chemist to speak of the weight of an atom without stating to which element he referred. The magnitude of a quantum of radiation depends upon the wave-length (frequency) of the radiation. The relation between the masses of the atoms of different elements is a complex one, but that between the magnitudes of the quanta of radiations of various frequencies is the very simple one of direct proportionality. The frequency of the radiation multiplied by a constant gives the energy per quantum of that radiation. In most physical literature the frequency is denoted by the Greek letter ν and the constant by h. Therefore, the energy ϵ of a photon of radiation of a given frequency ν is given by

$$\epsilon = h\nu$$

This means that the constant h can be expressed by $h = \epsilon \times \frac{1}{\nu}$, that is, energy multiplied by the reciprocal of a frequency, which is the period or time of a vibration. The unit in terms of which h is measured is then one of energy multiplied by time, or erg seconds. The value of h has been determined by many methods to be 6.55×10^{-27} erg sec. The erg second is called by physicists a unit of action, this term being used to denote the product of energy and time.

When the quantum constant h is multiplied by the very large number which expresses the frequency of green light, the resulting energy is found to be still a small number, 3.93×10^{-12} erg. This is nevertheless of such an order of magnitude that its effects in producing discontinuities in radiation are discernible by physical methods. The quantum of energy associated with a line at 5890A would be 1.6×10^{-16} erg greater than that associated with one at 5891A.

Continuous and Line Spectra

The spectrum produced when the radiation emitted by a glowing solid is passed through a prism blackens a photographic plate continuously and rather uniformly. An additional effect is produced when gases or vapors at high temperatures emit light. In 1829, Sir John Herschel examined the spectra of the colored light produced by heating certain salts in an alcohol flame and found the emitted energy to appear concentrated in lines corresponding to relatively few wave-lengths. Such spectra are called line spectra, or discontinuous spectra. The wave-lengths at which such lines occur characterize the elements the vapors of which produce them when heated. Bunsen and Kirchhoff employed these bright-line spectra in the detection of those elements which emit lines under these conditions. In the preceding chapter, it was noted that the Fraunhofer black lines which cross the spectrum of sunlight are due to the absorption of certain lines by elements present in gaseous form in a layer surrounding the sun. The positions of these black lines on the wave-length scale correspond to the positions of the bright lines emitted by the same elements when heated and viewed directly. The identification of the Fraunhofer lines with those emitted by elements in the laboratory provided the means by which it became possible to determine which elements are present in the reversing or absorbing layer of gas surrounding the sun.

The bright line emission spectra of the elements consist, when viewed through a spectrograph, of a series of lines separated by regions of comparative darkness. They are produced as the result of processes occurring in widely separated atoms or molecules of substances in the vapor or gaseous state. The same processes occur also in the atoms or molecules comprising incandescent solids, but in this case any natural frequencies of rotation or vibration associated with these atoms or molecules are masked by effects produced by the continuous bombardment of neighboring atoms or molecules. The result is that the spectrum is continuous and yields no information in regard to the nature of the atoms or molecules present in the incandescent solid. As indicated in Figure 2, the predominating frequency is, instead, a function of the temperature. Some exceptions to this statement may be noted. The rare earths used in the Welsbach gas mantle, when heated to incandescence, emit line spectra. Nichols[7] described ten or more crests on the brightness curve of glowing neodymium oxide, which, however, bear no relation to the true line emission or absorption spectra of this compound. The theory of the origin of this type of spectrum has recently been discussed by Van Vleck.[8] Grain size influences the nature of the temperature radiation from other metallic oxides.[9]

Just as certain incandescent solids give indications of line spectra superposed on their continuous radiation, so conversely gases or vapors produce beneath their characteristic line spectra a more or less faint continuous background. Its origin has been attributed to the effects of free electrons of varying kinetic energies joining with ions to produce atoms or, in the case of molecules, to recombination of free atoms possessing varying kinetic energies. (See Chapter 9.)

There are two kinds of line spectra, those emitted by atoms and those emitted by diatomic or polyatomic molecules. The latter spectra, *i.e.*, molecular spectra, were called band spectra by the earlier spectroscopists whose apparatus of low resolving power revealed them only as a number of bands of light and darkness often overlapping to produce a channeled or fluted appearance. With more modern equipment they have been resolved into groups of lines. Molecular spectra will be reserved for discussion in Chapter 13; the remainder of the present chapter will be devoted to a consideration of the order underlying the positions of the lines in atomic spectra, and the theories of the mechanism of emission of radiation which have been devised to account for it.

The photochemist needs to know something of the theory of line spectra for two reasons. In the first place, his sources of radiation are predominantly means for treating gases or vapors of elements so that they emit line spectra. (In most sources the line spectra are somewhat complicated by the incidental production of some molecular spectra.) The lines which carry the radiant energy are at first sight spaced quite at random, and the intensities of different lines vary greatly in an apparently irregular manner. If it is desired to carry out a reaction by energy of wave-lengths between 2500 and 2600A, it is necessary to know which sources emit line spectra having strong lines located within this region. If, on the other hand, one wishes to test the action of the region of 2800-2900A, a source must be chosen having strong lines in that region, and only faint ones, if any, in the 2500-2600A region.

In the second place, the photochemist must understand the process by which molecules absorb energy. Since this is the converse of the process by which they emit molecular spectra and is quite complicated, it may best be approached after

[7] Nichols, E. L., *Proc. Nat. Acad. Sci.*, **11**, 47 (1925); *Chem. Abs.*, **19**, 1376 (1925).
[8] Van Vleck, J. H., *J. Phys. Chem.*, **41**, 67 (1937).
[9] Liebmann, G., *Z. Physik*, **63**, 404 (1930); Skaupy, F., *Physik. Z.*, **28**, 842 (1927).

the principles regarding the emission of atomic spectra are understood. Furthermore, the theory of atomic spectra itself represents one of the most important contributions which the students of the physics of ultraviolet radiations have made to chemistry, for it was the work of the spectroscopist which laid the foundation upon which have been erected the present theories of atomic structure.

Classification of the Lines in Atomic Spectra into Series

The spectrum of hydrogen, as obtained in a Geissler tube, consists of comparatively few lines. One is red, one blue, two are violet and many lie in the ultraviolet region. (Figure 3.) They are spaced far apart in the visible and approach

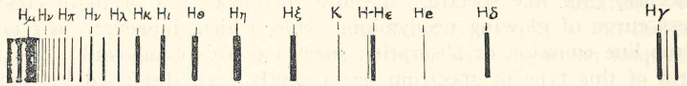


Figure 3. Balmer Series. (Eldridge, "Physical Basis of Things," New York, McGraw-Hill Book Co.).

each other more closely as the region of higher frequencies is approached. They occur at 6563, 4861, 4340, 4102, 3970, 3889, and 3825A. About 31 of these lines are recognized, piling up more closely to each other to reach a limit at 3646A. These lines are called the Balmer series after the scientist who showed in 1885 that the frequencies of the first nine lines could be expressed by a simple mathematical equation implying an underlying regularity.

Rydberg employed a more general expression which in a modified form applies to many elements. In the simplified form applicable only to hydrogen, it is

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where n_1 and n_2 are integers, n_2 being the larger, ν is the frequency of one line in the hydrogen spectrum, and R is a constant. By letting R be 109,737, n_1 be 2 and n_2 be successively 3, 4, 5, etc., the successive values of ν given by this expression correspond to the observed frequencies of the spectral lines of Balmer, expressed in wave-numbers. It is to be noted that the wave-number (or frequency divided by 3×10^{10}) is given by this expression as the difference between two terms. If the second term is nearly as large as the first, as when n_2 is only one unit greater than n_1, the difference between the two terms or the frequency of the line, is small, and the line lies in the red region. Since n_2 is in the denominator, an increase in its value will lower the value of the second term, making its difference from the first term greater and thereby increasing the frequency of the corresponding line. Successive increments of n_2 increase the frequencies of the corresponding lines by progressively smaller amounts. When n_2 becomes infinitely great, the second term disappears and the expression reduces to the frequency of the first term. This is, therefore, the limit of the series.

If, now, the calculation is repeated, this time starting with 3 for n_1 and 4, 5, 6, etc. for n_2, a new series of frequencies approaching a different limit will be obtained. The frequencies are such that these lines fall in the infrared region. This series of lines was discovered by Paschen in 1896. By starting with 4 for n_1 still another series of lines can be obtained; its limit lies still farther out in the infrared. Lines of this series were discovered by Brackett in 1922. When n_1 is made equal to one, the equation yields a series of lines in the ultraviolet. Most lie far out in the difficultly accessible region; they were discovered by Lyman.

Theory of the Mechanism of the Emission of Line Spectra

The Hydrogen Spectrum. The fact that the frequency of a spectral line is related to the difference between two terms was long a source of difficulty to the theorists who conceived of the spectral frequencies as in some manner related to natural frequencies of intra-atomic vibrations. The spectra of more than twenty elements had been resolved, at least in part, into series when Bohr in 1913 successfully employed the quantum theory of Planck in accounting for the origin of the lines in series spectra of the elements. He applied the new and almost unaccepted idea of the discontinuity of "action" to the dynamics of the structure of the atom as pictured by Lord Rutherford. In Rutherford's theory an atom is composed of a central positively charged nucleus around which there revolve in closed orbits as many electrons as are required to balance the positive charge of the nucleus. The positive charge of the nucleus as well as the number of electrons is equal to the atomic number of the element. The hydrogen atom consists of one electron revolving around a nucleus of equal and opposite charge. In helium, there are two revolving electrons, in lithium three, in carbon six, and so on to uranium with 92 electrons.

Although the orbits of the electrons are conceived as elliptical, it is perhaps simpler to regard them as circular in an introductory consideration of the theory as it applies to hydrogen. The electrostatic force of attraction between the electron and the oppositely charged nucleus balances the centrifugal force of rotation of the electron and so holds it in its orbit. A difficulty arises when the radiation of energy by such a system is considered. Motion in a circle is accelerated motion. It is fundamental in electrodynamics that an accelerated charge radiates energy, and the electron would be expected to spiral in gradually toward the nucleus. Actually, however, the spectroscopist knows that an atom emits no measurable radiation unless energy is supplied to it in some manner as by mechanical impact, by heat or by an electrical discharge.

The discrepancy between the experimental results and those expected on the basis of electrodynamics was as serious as that encountered in the study of black body radiation, which Planck had met by making the radical assumptions of the quantum theory. Bohr met the difficulty in the same manner by adopting the theory of Planck. He assumed it possible for the electron of the hydrogen atom to revolve, without radiating energy, in certain discrete orbits in which its angular momentum mvr (m is the mass of the electron, v its angular velocity, and r the radius of the orbit) is an integral multiple of $h/2\pi$, that is, $nh/2\pi$. By using known values of the mass and charge of the electron, it was possible to calculate from this quantum condition and an equation relating the centrifugal force and the electrostatic force between the electron and the nucleus, the radii of the orbits in which the electron could move without radiating energy. These were found to have radii of 0.5, 2.0, 4.5 and 8A, when n, called the quantum number, had the successive values 1, 2, 3 and 4. The radii of the permitted orbits increase as the squares of the quantum numbers. Each such orbit represents a state in which the hydrogen atom possesses a calculable amount of energy. Thus the atom may exist in definite energy states, or may be said to possess definite energy levels.

Bohr assumed that energy is radiated only during the time in which the electron falls from an orbit in which the atom has greater energy to one in which it has lesser energy; that is from an outer to an inner orbit. The energy emitted is the

difference between the energies possessed by the atom in the initial and final states. The transition may be either between adjacent or more widely separated permissible orbits or energy states. In terms of the quantum thory, the energy radiated is expressed by $h\nu$. Therefore, the difference between the energies in the initial and final states when divided by h yields the frequency of the line emitted.

It appears, therefore, that in the Bohr theory the frequency of the emitted line is not directly related to that of any vibration in the atom before or after emission, but to a difference between the energies possessed by the atom before and after emission. Emission from an atom persists for but a very brief period. The persistence of the lines seen to be emitted from a discharge tube is due to the successive emissions of the line by different ones of the great number of atoms in the tube. Of these, some at a given moment are in the resting state, others are being excited by the electrical discharge as a preliminary to emission, others are in the excited state in which the atom holds the energy acquired during excitation, and still others are emitting the observed line. Bohr's theory affords an explanation of the fact that in the Rydberg formula the wave-number of the emitted line is represented as the difference between two terms.

In terms of this theory, the various sources of ultraviolet light are devices for introducing energy into atoms (or sometimes molecules) in order to raise them to higher energy levels. This process is called excitation. In the Bohr picture, this consists of shifting an electron from an inner orbit, in which its potential energy has the greatest negative value, to an orbit of greater radius. The excited atoms have but a very transient existence, usually of the order of 10^{-8} second, after which the electron drops to an orbit of lower energy, which may or may not be the innermost orbit. It is during this process that a spectral line is emitted.

A transition of an electron from the second to the first energy level is accompanied by the emission of the first line of the Lyman series of hydrogen lines in the ultraviolet. An atom in which the electron transition is from the third to the first energy level emits the second line, one from the fourth to the first level emits the third line, and so on. The differences in energy in the successive energy levels lessen as n becomes large. Therefore, the differences between these higher levels and the resting level differ less and less as n becomes large and the successive lines of higher frequency occur closer together as the limit for infinite n is approached.

It is by no means always the case that the electrons fall back from higher levels to the resting level or innermost orbit. When they fall back only to the second level, the lines of the Balmer series are produced. Transitions to the third level gives the lines of the Paschen series. These statements follow directly from the Rydberg formula, the number used for n_1 giving the orbit to which the electrons drop during emission.

It may not be apparent why thirty or more lines of the Balmer series are seen simultaneously in the emission from a discharge tube. In any source there is present a tremendous number of atoms, some moving with high and some with low velocities, and others at rest. When such a mass of atoms is excited by the passage of an electrical discharge, there are differences in the states of excitation attained by different atoms. Some are excited to the second, and others to various other energy levels, even very high ones. Each atom then emits in a manner depending upon its state of excitation. When the radiation from the whole collection of emitting atoms is viewed through a prism, the lines resulting from each of the many types of transition in progress in different atoms are seen simultaneously. The relative intensities of the lines are related to the probabilities

with which the excited states giving rise to the lines are produced under the experimental conditions of excitation.

Elements Other Than Hydrogen. In the case of other elements, the line spectra are much more complex. In the iron spectrum, there are thousands of finely spaced lines. King[10] has recorded more than 3000 lines in the cerium spectrum, 1600 of which lie between 3000 and 4700A.

In the case of the spectra of the alkalies, it was found possible to classify the lines, at first by their distinctive appearances, into four series. Three of these were named by Rydberg the principal, sharp and diffuse series. A fourth series, discovered by Bergman in the infrared region, was called by Hicks the fundamental series, for reasons no longer pertinent. The descriptive significance of these names is not maintained in the case of more complex elements but because of their historical significance they have been generally retained and their abbreviations, P, S, D and F, are in common use in the designation of spectral terms.

The Rydberg formula for the frequencies of the lines of a series for the alkalies differs from the simplified form applicable to hydrogen in having two additional constants, μ_1 and μ_2:

$$\nu = R\left(\frac{1}{(n_1+\mu_1)^2} - \frac{1}{(n_2+\mu_2)^2}\right)$$

These constants have fractional values characteristic of the elements. These differ also for lines of the sharp, principal, diffuse and fundamental series of a given element. In the case of sodium, when μ_1 is 0.626 and μ_2 is 0.13, the expression, using $n_1 = 1$, gives the lines of the principal series. If n_1 is taken as 2 and the μ_1 and μ_2 values are reversed, the lines of the sharp series are given. By replacing μ_2 by a new constant, $\mu_3 = 0.99$, in the second term, the lines of the diffuse series are obtained. By making $\mu_1 = 3$, using μ_3 in the first term and still another constant $\mu_4 = 0.999$ in the second term, the infrared lines of the Bergman or fundamental series are found. These four constants, known also as "defects," are only approximations, and the lines are never given as exactly as is the case with the simplified expression for hydrogen in which "defects" may be neglected in all but the most accurate work.

The existence of these "defects" and the resulting occurrence of lines of sharp, diffuse, principal and other series, implies that the energy states of the alkali atoms cannot be sufficiently characterized by the single quantum number n. A second number L is required to distinguish the energy levels which exist. In the earlier development of the theory it was assumed that this was due to the fact that the orbits were elliptical rather than circular. Electrons moving in such orbits would have, in addition to a rotary motion about the focus at which the nucleus is situated, a radial motion toward and from the nucleus. For each of these forms of periodic motion quantized energy states were postulated. This increased the number of energy levels, since for each n value there may be several L values. In general, the energy differences between L states with the same n value are less than those between the states with successive n values. It has been found that L, called the orbital quantum number, may have the value zero, or any integer up to one less than the value of n.* An energy level or term for

[10] King, A. S., *Phys. Rev.*, **29**, 366 (1927).

* It is unnecessary to discuss in detail the history of the development of the theory of these quantum numbers or of others since introduced. They were first arrived at by an extension of the Bohr theory by Sommerfeld, but have subsequently been found to emerge naturally from the theories of quantum mechanics.

which L is zero is an S term, one for which it is 1 a P term, one for which it is 2 a D term, and one for which it is 3 an F term.

As in the case of the Bohr theory of the hydrogen atom, the spectral lines result from transitions from higher to lower energy levels. Not all of the theoretically possible transitions between terms are found to occur under the usual experimental conditions, or, as the spectroscopist would express it, not all terms combine to give lines. It has been found possible to predict which transitions may occur by the aid of certain *selection rules*. These were originally obtained empirically, but have since been found to have a theoretical basis. One selection rule states that, in absorption or emission, L must increase or decrease by one. In other words, transitions may occur only between states whose L values differ by but one unit. S states can undergo transitions only to or from P states, but P states may combine with either S or D states, D states with P or F states, and so on. Other transitions are said to be forbidden. Selection rules are not, however, absolutely binding, since under certain conditions, lines corresponding to transitions other than those given by the rules may appear with low intensities. Thus, the term *forbidden* is a misnomer, since forbidden lines are really lines corresponding to transitions of only low probability. The quantum mechanics affords methods for calculating the probability of transitions.

There is no selection rule limiting the number of integers by which the principal quantum number n may change in a transition.

Spectroscopists denote a spectral line by writing the terms separated by a dash. In writing the terms the abbreviations S, P, D, etc. are used to indicate the L value of each; these are preceded by numerals for the n value of each. Thus a line of the principal series may be written 1S-2P, or in general, 1S-nP, successive values of n giving the successive lines of the series. Lines of the sharp series are given by 2P-nS, those of the diffuse series by 2P-nD, of the Bergman series by 3D-nF. The symbol of the last term refers to the series of which the lines are members. The first term gives the limit of the series. The sharp and diffuse series of lines of the alkalies approach the same limit, depending upon whether L increases or decreases by one in falling from a state of greater to one of lesser energy.

Further complications arise when the processes of emission or absorption occur in a magnetic field. Under these conditions, a given line may be split into several lines (Zeeman effect). Even without the application of a magnetic field, certain lines of the alkalies, *e.g.*, the D line of sodium, may be observed to be resolved by a spectroscope into two closely adjacent lines, called a doublet. In the case of elements of other groups of the periodic system there may be triplets, quadruplets and even higher degrees of multiplicity, thus greatly complicating the spectra. In some cases, the corresponding lines of multiplets may not lie close together but may be hundreds of Ångström units apart and be separated by great numbers of intervening lines.

These effects may be accounted for by considering that the terms are split into others of but slightly different energy levels. Thus, to characterize the greater number of terms implied, a third quantum number, J, called the inner quantum number, is employed. In writing the terms, the value of J is placed as a subscript to the right, as in $1S_{1/2}$, $2P_{3/2}$, etc. The multiplicities of the terms are indicated by upper left indices, as in $^3D_2$.[11] A selection rule states that J may either increase

[11] For a discussion of this notation, see Russell, H. N., Shenstone, A. G., and Turner, L. A., *Phys. Rev.*, **33**, 900 (1929).

or decrease by one, or need not change in a transition, except that in cases in which it is initially zero, it must change.

The multiplicities exhibited by an element depend upon its position in the periodic table and must, therefore, be related to the electronic configuration of the atom. The terms of atoms with an even number of electrons have odd multiplicities. Those of atoms with an odd number of electrons have even multiplicities. Elements of the alkalies have doublets, those of the alkaline earths singlets and triplets, those of the next group doublets and quartets, and those of the next group singlets, triplets, quintets, etc.

Many attempts have been made to arrive at a physical interpretation of these features of the spectral terms by extending the Bohr theory to atoms having more than one electron. These take into account the interactions between the electrons, and involve complexities of interest chiefly to the specialist in atomic spectra.[12] It need only be mentioned here that this development showed the need of a new concept—the electron spin—introduced by Uhlenbeck and Goudsmit[13] and by Bichowsky and Urey.[14] This assumes each electron to rotate about its own axis besides moving in an orbit about the nucleus.* The electron spin has an angular momentum $1/2\, h/2\pi$.

The effects of the spins of the electrons in the atom (only the valence electrons or those outside the kernel need be considered) may be lumped together by the methods of vector analysis into a resultant spin vector S for the atom. This assumes only certain discrete values. If all the spins are parallel, S is equal to one-half the number of electrons since each contributes 1/2. The contributions of antiparallel electrons neutralize each other. For example, if as in the alkaline earths, there are two electrons outside the kernel, S will be one if the spins are parallel and 0 if they are antiparallel. The extreme values which the quantum number J may possess for a given L level for a given atom are obtained by adding L and S and by subtracting S from L. J may also have all intermediate values which differ from these extreme values and from each other by integers. This means that if L is greater than S, the number of J values for a given L (the multiplicity of the term) is given by $2S+1$.

It must now be emphasized that the Bohr theory, although useful in stimulating the earlier development of the theory of spectra, had many arbitrary features and, indeed, probably was in error in certain features. The quantum numbers and selection rules have subsequently been shown to emerge more logically from quantum mechanics. The methods employed require a degree of mathematical

[12] For accounts of these see books on atomic spectra. The following have been consulted in preparing this brief summary: Johnson, R. C., "Spectra," London, Methuen, 1928; Herzberg, G., "Atomic Spectra and Atomic Structure," New York, Prentice-Hall, 1937; White, H. L., "Introduction to Atomic Spectra," New York, McGraw-Hill, 1934; Candler, A. C., "Atomic Spectra and the Vector Model," 2 Vols., Cambridge Univ. Press, 1937. An exhaustive bibliography has been given by Gibbs, R. C., *Rev. Modern Physics*, **4**, 278 (1932).

[13] Uhlenbeck, G. F., and Goudsmit, S., *Naturwiss*, **13**, 953 (1925); *Nature*, **117**, 264 (1926); see also Compton, A. H., *J. Frank. Inst.*, 145, *1921*, Aug.

[14] Bichowsky, F. R., and Urey, H. C., *Proc. Nat. Acad. Sci.*, **12**, 80 (1926).

* The state of each individual electron in an atom can be described by four quantum numbers. n the principal quantum number, l the orbital quantum number, m_l the magnetic quantum number, and m_s the electron spin number. n can have any integral value, l can have any integral value up to one less than n, m_l may have any integral value between l and $-l$, including zero, (or a total number of possible values equal to $2l+1$), and m_s can have only the values $-1/2$ or $+1/2$. Pauli's exclusion principle states[15] that no two electrons in the same atom can have all four quantum numbers the same. This principle and the restrictions on the values which the quantum numbers may possess permit the description of the electron configurations of the atoms of all the elements of the periodic table. Fowler states[16] that it is possible to predict from the electron configuration of an element, however complex, the main features of its spectrum.

[15] Pauli, W. Jr., *Z. Physik*, **31**, 765 (1925).

[16] Fowler, A., *J. Chem. Soc.*, **1928**, 777.

training possessed by relatively few chemists and must be sought in special texts. This development has arisen from the work of Heisenberg [17] on matrix mechanics and independently from the introduction by Schrödinger [18] of the wave equation of De Broglie [19] into the classic equation for the propagation of elastic waves. The result of the latter approach was a differential equation which could be applied to the motion of the electron in the hydrogen atom. This equation has a discrete set of solutions called *eigenfunctions* which represent energy states of the atom. According to these theories, the electron orbits of the atom have lost their once-assumed definiteness and it is possible only to calculate the probability of an electron being found within a definite minute volume of space. They do, however, confirm the existence of definite energy levels, transitions between which give rise to the spectral lines. Indeed, it may be said that although the Bohr theory had assumed their existence, their occurrence was nevertheless inexplicable and, until the advent of the quantum mechanics, marked a sharp break with all previous conceptions of electrodynamics.

Experimental data confirming the existence of definite atomic energy states are now abundant. The stepwise excitation of atoms by the impacts of electrons carrying definite amounts of kinetic energy was mentioned in Chapter 1. This stepwise production of various spectral lines in succession has, since the pioneering experiments of Franck and Hertz, been carried out in the case of many elements. For example, Schulze [20] has excited argon in seven stages. The method offers great experimental difficulties and the literature contains many discrepancies in the values assigned to the various resonance potentials of the elements by modifications of this method.

The various spectral lines or groups of lines may be also produced in an analogous step-wise manner by carefully controlled thermal excitation of the elements. In the Pasadena laboratory of the Mt. Wilson observatory, King volatilized the metals in a graphite tube electrically heated in a specially designed furnace to temperatures not far below that of an electric arc. He showed [21] that calcium vapor yields a line at 4227A at relatively low temperatures, and that lines at 3969 and 3934A appear only at temperatures above 2400°C. He has also given [22] temperature classifications of the lines of strontium, barium, magnesium, iron, titanium, vanadium, chromium, cobalt, nickel, manganese, scandium and many other elements. In the case of iron, he has grouped 902 lines according to their occurrence or absence when the temperature is 1600-1700°C., 2000°C., or 2500-2600°C. Only eleven lines are emitted at 1400°C. The method, which has also been employed by others,[23] is chiefly of value to the spectroscopist as an aid in classifying the lines into various series.

Production of Ions in Ultraviolet Sources

The chemist is familiar with ions produced as the result of electrolytic dissociation in aqueous solutions. The physicist, however, frequently encounters ions in the gaseous state, since by the application of high temperatures, electric discharges or certain radiations, it is possible so strongly to excite an atom that one or more of its electrons is sent to an orbit extremely far from the nucleus. Since the attractive force of the nucleus becomes insufficient to hold the electron in a far distant orbit, it becomes lost to the atom, and shoots out into space where, as a minute particle, it behaves as an independent unit, and is one of the particles making up an "electron gas." The atom which has lost the electron or electrons is called an ion.

[17] Heisenberg, W., *Z. Physik,* **33,** 879 (1925).

[18] Schrödinger, E., *Ann. Physik,* **79,** 361, 489, 734 (1926); *Phys. Rev.,* **28,** 1049 (1926).

[19] De Broglie, L., *Phil. Mag.,* **47,** 446 (1924); *Ann. de Phys.,* **3,** 22 (1925).

[20] Schulze, B., *Z. Physik,* **56,** 378 (1929).

[21] King, A. S., *Astrophys. J.,* **28,** 389 (1908); **29,** 381 (1909).

[22] *Ibid.,* **29,** 190 (1909); **48,** 13 (1918); **51,** 179 (1920); **37,** 239 (1913); **56,** 318 (1922); **39,** 139 (1914); **59,** 155 (1924); **41,** 86 (1915); **60,** 282 (1924); **42,** 344 (1915); **53,** 133 (1921); **54,** 28 (1921); **65,** 86 (1927); **89,** 377 (1939).

[23] Paton, R. F., and Rassweiler, G. M., *Phys. Rev.,* **33,** 16 (1929); Ritschl, R., *Ann. Phys.,* **13,** 337 (1932); Schüler, H., *Z. Physik,* **37,** 728 (1926).

The work necessary to remove an electron from an atom is greater than that required to displace it to any of the hypothetical orbits representing the stationary energy states of the atom. It is the ionizing work; when expressed in electron-volts, commonly shortened to volts, it is called the ionization potential. It is greater than any of the potentials corresponding to the excited states. In the case of mercury, it is 10.4 volts.

To ionize an already excited atom requires less work than is needed in the case of an atom in its stable state. To ionize a hydrogen atom which is already excited to a high energy level requires less energy than to ionize one excited only to a lower energy level. The difference between the amounts of energy required for ionization in these two cases represents the amount of energy required to raise the atom from the lower to the higher stage of excitation. This would be the amount of energy emitted in a spontaneous return of the atom from the higher to the lower energy level. By multiplying the frequency of the emitted line by the Planck constant, the value of this energy is obtained in ergs.

By both the spectroscopic method and the method of studying the effects on atoms of impacts of electrons accelerated by electric potential gradients, physicists have obtained a large amount of information regarding the energies required to excite atoms of most of the elements to various energy levels, or to ionize them. The detailed results have been summarized by Bacher and Goudsmit.[24] The ionization potentials of a few of the elements most frequently employed in sources of ultraviolet rays are given in Table 1, which also includes for some a resonance potential and the energy required to expel a second electron from an ion of the atom.

Table 1.—Resonance and Ionization Potentials of Various Elements.

Element	Resonance Potential (volts)	Ionization Potentials of Atom. (volts)	Ion.
Hydrogen	10.4	13.5	....
Helium	20.4	24.46	....
Carbon	....	11.2	24.3
Nitrogen	8.2	14.5	29.5
Neon	11.8	21.5	40.9
Sodium	2.1	5.1	....
Argon	13.2	15.7	27.8
Mercury	4.9 (6.67)	10.38	18.65

Energy-Level Diagrams. The transitions permissible between the energy states of an atom are most readily set forth in diagrams called energy-level diagrams or Grotrian diagrams.[25] These serve also to indicate the energies in the various levels. Such a diagram for mercury is given in Figure 4.

A horizontal line at the top of the diagram represents the energy of the ion,

[24] Bacher, R. F., and Goudsmit, S., "Atomic Energy States," New York, McGraw-Hill Book Co., 1932.

[25] Grotrian, W., "Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei, und drei Valenzelektronen," 2 vols., Julius Springer, Berlin, 1928.

which is arbitrarily taken as zero. A dot placed near the bottom of a vertical line at the left of the diagram indicates the energy of the stable or normal state of the atom. The distance at which it is located below the zero energy state of the ion on a suitable scale represents the energy which must be put into the atom to ionize it. Since the atom in its normal state has less energy than the ion, which is arbitrarily taken as zero, the energy associated with the atom or with any state of excitation less than ionization, is considered to have a negative value. The energy values are frequently expressed in electron-volts, since in many cases the

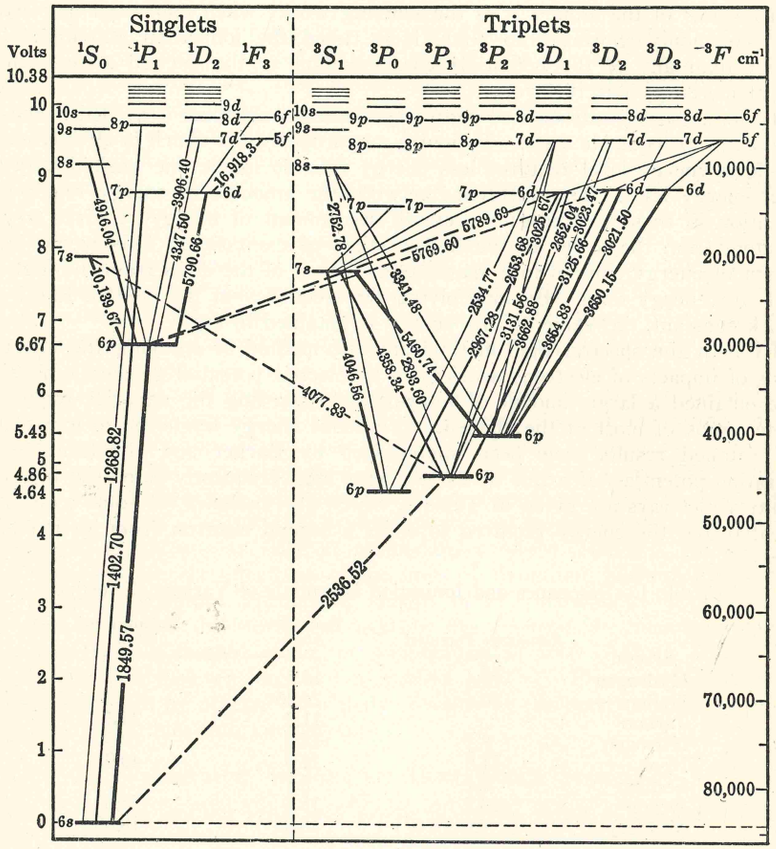


FIGURE 4. Energy-level Diagram for Mercury (W. Grotrian, "Graphische Darstellung der Spektren von Atomen mit ein, zwei und drei Valenzelektronen," Courtesy of Julius Springer, Berlin).

information was obtained by the method of critical potentials. As the diagram is also intended to yield the frequencies of lines emitted during transitions from one state to another, it is convenient to employ also a vertical scale giving the frequencies corresponding to the various energy states. This can be obtained by dividing the energies in ergs by Planck's constant h. Division by the velocity

of light converts these frequencies into the more convenient wave-numbers. Usually, the levels are determined spectroscopically by multiplying the wave-number of the line by hc to obtain the increment of energy between the energy levels.

Energy-levels for each of the S, P, D and F terms are designated by short horizontal marks. Doublets, triplets, etc. are indicated by using separate columns for each member of the multiplet. The state of excitation for each electron is usually denoted by giving the principal quantum number as a numeral for each short horizontal line marking an energy state.

Diagonal lines are drawn connecting the various states in accordance with the selection principles. The difference between the wave-numbers of the states connected by a diagonal line yields the wave-number of the spectral line. Transitions between terms of unequal multiplicity are called intercombination lines. They violate the selection rule that when J is 0, its value must change. It happens, however, that the prominent mercury resonance line, 2537A, is such an intercombination line.

Chapter 3

Survey of Sources

The various sources of ultraviolet radiations are all devices for the application of energy to atoms and molecules, usually in the vapor or gaseous states, for the purpose of exciting them to higher energy-levels. The differences between the many types of apparatus lie in the choice of the atoms which are excited, in the form of energy applied for the excitation, and in the means adopted for its application.

Once the excitation has been effected, the excited atoms or molecules retain their increments of energy for a brief period and then revert to states of lower energy, emitting their extra energy as radiation. The duration of the excited states may be altered somewhat by varying the pressure of the gas or by adding an inert gas.

The natural source of radiations, the sun, is discussed in Chapter 11, following a consideration of filters, since atmospheric filtration prevents some of its radiations from reaching the surface of the earth. The most important artificial sources of ultraviolet rays are the arc, spark and glow discharge. In the following paragraphs the chief points of distinction between these types of discharge will be described, after which other less widely used sources will be considered.

The passage of a direct current discharge through gases at low pressures frequently gives rise to the glow discharge, the well-known phenomenon observed in a Geissler tube. In it, various parts of the tube assume characteristic appearances known as the cathode glow, the Crookes dark space, the negative glow, the Faraday dark space, the positive column and, when present, the anode glow.

The arc is a discharge of electricity through a gas, which may be at any pressure, under conditions such that one or both of the electrodes becomes heated and by vaporization contributes a stream of gaseous material which aids in the conduction of the current (direct or alternating) across the space. In these two forms of discharge—the glow and the arc—the impressed voltage is usually low, as compared with the very high voltages employed for the spark discharge. In the arc, the potential drop in the region of the cathode is usually very low, of the order of tens of volts, but in the glow, it is of the order of hundreds of volts. In practice, the spark usually involves the very brief oscillatory discharge of some form of condenser across an air-gap, with the production of light and heat. With suitable equipment, a series of very rapidly repeated discharges may occur with the production of a loud sound.

Close to the cathode in a glow discharge in nitrogen at 0.5 mm. pressure [1] is a narrow dark space (Crookes dark space), followed by an intense negative glow region which decreases in intensity to the Faraday dark space, several times wider than the cathode dark space. This is followed by the bright positive column which begins sharply at a definite position and extends, usually with uniform intensity, toward the anode. Under certain conditions, the positive column may be striated. There may also be an anode glow. The positions between the

[1] This discussion of the glow discharge is based upon one by Dushman, S., *Elect. Eng.*, **53**, 1204, 1283 (1934); see also Found, C. G., *Trans. Illum. Eng. Soc.*, **33**, 161 (1938).

boundaries of these various regions are determined by the cathode, since they are changed if the cathode is moved within the discharge tube but are not affected by moving the anode. If the anode is made to approach the cathode, the length of the positive column decreases. It is possible to eliminate the latter completely and have the anode located within the negative glow or in the cathode dark space.

The potentials with respect to the cathode at various points may be determined by the use of exploring wires or electrodes introduced into the various regions, a method employed by Stark, Retschinsky and Shaposchnikoff [2] and placed upon a sound theoretical foundation by Langmuir and Mott-Smith.[3] The use of this "probe" method has been of great value in advancing our knowledge of the mechanisms occurring in gaseous discharges, as it is capable of yielding information as to the potential distribution, the densities of ions and the mean kinetic energies of the free electrons.

Close to the cathode is a narrow region in which there is a steep potential gradient, the drop varying from 60 to 400 volts, depending on the nature of the gas and the cathode. Much of the entire discharge voltage drop occurs in this region. In the Faraday dark space there may be a slight positive or even a negative gradient. Throughout the positive column, the gradient is constant, so that the total voltage drop in the tube depends upon the length of the positive column as well as upon the cathode fall. In the glow discharge, there is little change in voltage at the anode. Compton and Morse [4] assume the large amount of energy consumed in the cathode fall to be used in accelerating positive ions toward the cathode. By bombarding the cathode, these liberate electrons; the liberated electrons while close to the cathode receive enough energy to enable them on striking atoms to produce more positive ions, and so continue the process. These authors calculate that an electron makes about ten such ionizing collisions in passing through the region of the cathode fall, and consider that most of the current at the surface of the cathode is carried by positive ions.

The large drop of 300 or more volts in this region may be lessened by employing some accessory method of inducing the cathode to emit electrons, such as heating it to produce thermionic emission or irradiating it with ultraviolet light to cause photoelectric emission. By such methods the cathode drop may be reduced to a value related to that of the ionization potential or of a resonance potential of the gas.

The remaining space between the electrodes is called the plasma, a term also used in the case of arcs. Langmuir [5] showed that the thickness of the cathode sheath is of the order of 0.01 mm. Electrons from the cathode are accelerated in this sheath and carry their energy into the plasma where most of the emission of light occurs. Electrons which have acquired the energy of the cathode drop V_c (electron-volts) are called primary electrons. Such a primary electron on striking a gas atom may lose to it by inelastic impact the energy required for ionization, V_I. It then has left the energy $V_c - V_I$ and is called a secondary electron. Its energy may still be sufficient to excite certain atoms, depending upon their resonance

[2] Stark, J., Retschinsky, T., and Shaposchnikoff, A., *Ann. Physik*, **18**, 213 (1905).

[3] Langmuir, I., and Mott-Smith, H. Jr., *Gen. Electric Rev.*, **27**, 449, 538, 616, 762, 810 (1924). For recent developments of the theory of the probe method, see Davydov, B. I., and Zmanovskaya, L. I., *J. Tech. Phys. (U.S.S.R.)*, **6**, 1244 (1936); Emeléus, H. J., and Brown, W. L., *Phil. Mag.*, **22**, 898 (1936); Polin, V., and Gvozdover, S., *Physik. Z. Sowjetunion*, **13**, 47 (1938); *Chem. Abs.*, **32**, 4422 (1938); Yankin, G. M., *J. Tech. Phys. (U.S.S.R.)*, **8**, 45 (1938); *Chem. Abs.*, **32**, 5692 (1938).

[4] Compton, K. T., and Morse, P. M., *Phys. Rev.*, **30**, 305 (1927). For recent observations on the cathode region, see Brewer, A. K., and Westhaver, J. W., *J. Applied Phys.*, **8**, 779 (1937); Günther-schulze, A., and Betz, H., *Z. Physik*, **108**, 780 (1938).

[5] Langmuir, I., *Phys. Rev.*, **33**, 954 (1929).

potentials. When the electron after such collisions no longer has enough energy to excite atoms by impact, it is called an ultimate electron.

Although in this discussion, it has been assumed that the cathode is cold and need not contribute any metallic vapor to the glow, it is possible under certain conditions to have a glow discharge from a molten cathode. Although the glow form of discharge is most commonly produced in gases at low pressures, nevertheless it may be produced under some conditions at atmospheric pressure if the current carried by the discharge is kept at only a few milliamperes. As the current is increased beyond a certain limiting value, usually about 0.1 ampere, the glow suddenly changes to an arc. In the arc discharge, the cathode current density is from a hundred to a thousand times that in the glow discharge, and the restricted spot from which the current issues may be very hot. It was for a time generally believed that high temperatures near, if not at, the cathode were essential for the maintenance of an arc.[6]

It has, however, been shown that the mercury-vapor arc can be operated with the cathode maintained at $-70°$C. or lower, the voltage being not much higher than in normal operation of the arc.[7] Apparently exceptions to general rules are so frequent and the number of borderline cases so great that rigid definitions of the forms of gaseous discharge are scarcely attainable. The following were suggested by Thomson:[8]

Glow. A discharge between cold electrodes, the current being carried entirely by gaseous ions and electrons.

Arc. A discharge in which the current is carried by the material of the electrodes as well as by the gas between them.

Spark. The initial unstable stage in any discharge between cold electrodes.

Spark and Arc Spectral Lines. The spectra produced by an arc and by a spark between similar electrodes may differ widely in character. An understanding of the origin of this difference, which is fundamental both historically and theoretically in the origin of atomic spectra, is essential to the employment of these sources in spectrographic methods for detection of the elements. Lockyer, a pioneer in solar spectroscopy, discovered that the intensities of certain lines occurring in the arc spectra of many elements are enhanced in their spark spectra.[9] In some cases, lines occurring in the arc spectrum are missing in the spark spectrum; on the other hand, the spark spectrum may show lines not present in the arc spectrum. Lockyer demonstrated the appearance of new or "enhanced" lines in the spectra of stars, particularly in the Novae, and believed that they indicated the existence of hitherto unknown elements capable of existing only at the enormous temperatures of the stars, or under the conditions of temperature found in the spark. It has since been shown that "spark" lines can also be produced by the high temperature excitation of certain elements in a resistance furnace.

The key to the nature of these assumed new elements was given in Bohr's earliest paper on the theory of atomic structure. In 1897, Pickering had discovered in the spectrum of a certain star, besides the Balmer lines of hydrogen, a series of new lines, each of which lay about midway between two lines of the Balmer series. Their frequencies could be represented by the Balmer formula if for 3, 4, etc. in the second term, there were substituted 3.5, 4.5, etc. As he believed

[6] For discussion, see Slepian, J., *J. Frank. Inst.*, **1926,** 79; *Phys. Rev.*, **27,** 407 (1926).

[7] Kawa, J., *Acta Phys. Polonica,* **1,** 427 (1932); Newman, F. H., *Phil. Mag.,* **18,** 607 (1934).

[8] Thomson, J., *Phil. Mag.,* **13,** 824 (1932); see also Mckeown, S. S., *Phys. Rev.,* **34,** 611 (1929) and Kaiser, H., and Wallraff, *Z. Physik,* **112,** 215 (1939) for transitions between the forms of discharge.

[9] Lockyer, Sir Norman, *Proc. Roy. Soc.,* **30,** 22 (1879).

the new lines to be due to hydrogen, Pickering altered the Balmer formula to include them by making the Rydberg constant four times its usual value. The new lines were not, however, encountered in spectra excited in the laboratory until Fowler in 1912 observed them in the spectrum of a discharge tube containing both hydrogen and helium. Bohr realized that if a helium atom should lose an electron the resulting ion would resemble the hydrogen atom, except for the fact that its nucleus would bear two positive charges rather than one. He appreciated the necessity of incorporating the number of nuclear charges, *i.e.,* the atomic number, in his equation for the calculation of the energy associated with the rotation of an electron in an orbit, the expression which in his theory yields the Rydberg constant. As this expression involves the square of the nuclear charge, the result yields a constant four times as great when there are two nuclear charges as when there is but one. The constant for the helium spectrum would, therefore, be four times that for the hydrogen atom. This led Bohr to suggest that the Pickering lines are emitted by helium ions rather than by hydrogen, an explanation which met with much opposition until it was found that the lines could be observed in pure helium when suitably excited.

It is more difficult to excite helium to emit the Pickering lines than it is to cause this element to emit the ordinary lines observed in the glow discharge. In order to form the ion and induce it to emit energy, spark excitation is used. In general, spectra of the ions of elements are commonly called spark spectra, as distinguished from the arc spectra from the atoms of the same elements. These designations must not be taken too literally, since the so-called "spark" spectra of many elements may be produced by other means of excitation. Some lines of a spark series frequently appear in arc spectra, although they may be enhanced in intensity in the spark spectra of the same elements.

It has been noted that the spark spectrum of helium resembles the arc spectrum of hydrogen, the preceding element of the periodic table, the only difference being that the Rydberg formula must be altered to take account of the extra nuclear charge. Similar relations hold throughout the periodic system. The alkaline earth elements have two electrons in the outer ring. Loss of one of these on ionization causes the atom to resemble that of the preceding alkali metal and to give a spectrum like it when the excess nuclear charge is taken into account. The multiplicities of the ions of elements are closely related to those of the atoms of the preceding elements of the periodic table.

It is also possible to observe under suitable conditions spectra from doubly charged ions, or atoms which have lost two electrons. In some instances, still higher degrees of ionization have been studied. To distinguish between these spectra, Roman numerals are employed after the symbol of the element. Thus, C I refers to the spectrum of the neutral carbon atom, C II to that of the ion C^{+}, C III to that of the doubly charged ion C^{++} and C IV to that of triply ionized carbon, C^{+++}. These are spectra of various orders, C I being of the first order. A given element excited by various methods produces different spectra, in each of which lines corresponding to one or another of these stages of ionization predominate. The demarcations are not sharp and it is common to find faint lines representing a higher degree of ionization superposed upon a spectrum of lines representing a lower stage of ionization. Antimony excited by a vacuum spark yields predominantly lines due to the doubly ionized atom Sb III. Tin in a Paschen hollow cathode in a discharge tube emits the lines of Sn II.[10]

[10] Lang, R. J., *Phys. Rev.,* **35,** 445 (1930).

In the atmosphere of the sun most of the elements are in the atomic state and yield the arc spectra. Spark lines are, however, observed in the case of a few easily ionized elements such as calcium. In the spectra of some stars, lines are found indicative of the presence of singly, doubly or further ionized ions. The appearance of lines of this character serves as a scale by which such bodies may be classified according to their temperatures. In the interiors of some of the stars, the temperatures reach millions of degrees and completely stripped atoms—mere nuclei—are believed to exist.

Other Sources of Ultraviolet Rays of Lesser Importance

Incandescent Solids. The Nernst glower is said to yield a faint spectrum even beyond 2500A. Not for many years, however, has it been employed as a source of ultraviolet rays.[11]

Since about 1920, the incandescent tungsten lamp, operated at an abnormally high filament temperature, has been employed occasionally as a source of continuous ultraviolet rays for absorption studies. Lamps intended for this purpose, and provided with special quartz bulbs or windows, were described by Gehlhoff,[12] Franck and Grotrian,[13] and by Stockbarger.[14] Also, Stockbarger, Dingee and Burns [15] have presented spectrograms showing that automobile headlight bulbs operated at a filament temperature of 3400°K. (at which they last but a few hours), permit the detection of radiations less than 3000A when the bulbs are of lead glass. With soda-lime glass bulbs, emission to 2900A could be detected, and measurements indicated that 0.046 per cent of the energy emitted through such bulbs lies below 3170A. As this was over three times the amount of radiation expected in this region from the laws of black-body radiation, they concluded that there is a selective ultraviolet emission.

Luckiesh [16] presented calculations of the percentages of the total emission which lie between 2800 and 3200A from tungsten filament lamps of various wattages at several temperatures. His results indicated that such lamps would not be very effective sources for supplying this band of radiations to children. For the same total energies a quartz mercury arc gives 175 times as great an output in this region as does a tungsten filament lamp. Later calculations by Forsythe and Christison [17] were more favorable. By utilizing data of Hulburt [18] on the percentages of the total emissivity at 3400, 3800 and at 4200A at various temperatures up to 2800°K. and employing certain considerations relating to the color temperature of tungsten, Forsythe and Christison obtained a curve for the spectral emissivity of tungsten at 2800°K. from the infrared to 2700A. By a step-by-step integration, they secured from this curve values for the relative amounts of energy in various portions of the spectrum. From these values (at several temperatures) and the total wattages of the lamps were calculated theoretical amounts of energy in these spectral regions falling upon a square centimeter of surface at a distance of one meter from the filament. The absence of any absorbing bulb surrounding the filament was assumed. It was found that a 500-watt tungsten lamp burning

[11] Coblentz, W. W., *Bur. Standards Bull.*, **9**, 103 (1913); Griffiths, H. D., *Phil. Mag.*, **50**, 263 (1925).
[12] Gehlhoff, G., *Z. tech. Physik*, **1**, 224 (1920).
[13] Franck, J., and Grotrian, W., *Z. tech. Physik*, **3**, 195 (1922).
[14] Stockbarger, D. C., *J. Opt. Soc. Am.*, **9**, 337 (1924).
[15] Stockbarger, D. C., Dingee, A. L., and Burns, L., *J. Opt. Soc. Am.*, **18**, 53 (1929).
[16] Luckiesh, M., *J. Frank. Inst.*, **206**, 60 (1928).
[17] Forsythe, W. E., and Christison, F., *General Electric Rev.*, **32**, 662 (1929).
[18] Hulburt, E. O., *Astrophys. J.*, **45**, 149 (1917).

under conditions giving a life of 1000 hours would yield a total energy of 4 milliwatts per square centimeter, of which 0.0013 milliwatt was of wave-lengths shorter than 3250A and 0.00044 milliwatt was between 3100 and 2900 A. When the lamp was burned under 100-hour life conditions, the values were, respectively, 4.00, 0.0017 and 0.00060. A 900-watt motion-picture lamp gave 9.2, 0.0076 and 0.0028 milliwatts. These values compared favorably with the energy of the sunlight passing through an air-mass of 2.37 atmospheres, which gave 0.010 milliwatt of energy shorter than 3250A and only 0.00017 between 3100 and 2900A. The total energy of the sunlight was, however, far greater, 33.9 milliwatts.[19]

Borstler [20] proposed the therapeutic use, by means of a quartz applicator, of ultraviolet radiations from a 6- or 8-volt tungsten automobile headlight in a Pyrex bulb, operated at voltages 10 per cent above normal.

Flames. As sources of ultraviolet radiations, flames are of little value. They are employed occasionally in conjunction with sparks in certain methods of quantitative analysis by spectrographic methods. In the early work in the visible region, flames were used as a ready means of vaporizing salts and exciting the metallic portions thereof, particularly the alkalies, which readily give characteristic lines.[21] To make the method available for the detection of elements more difficult to excite, higher temperatures are necessary. Early students of line spectra [22] secured these by directing an oxyhydrogen blowpipe upon the solid to be examined. Still higher temperatures may be attained with the aid of the oxyacetylene flame.[23] The spectrum produced in the flame itself is sometimes a complicating factor. It is a band spectrum emitted by the molecules of water vapor produced during combustion. The lines of these bands are weak at wave-lengths greater than 3200A and interfere but little with analyses based upon lines situated at longer wave-lengths.

Before the development of the mercury arc or the appreciation of the value of other simpler arcs, flames were occasionally employed as sources in the study of reactions produced by ultraviolet rays. Wulf employed a flame of carbon disulfide and oxygen for such purposes.[24]

Bombardment by α-rays [25] or cathode-rays [26] has been used in investigations in the region of wave-lengths longer than those of the usual x-rays.

Among the less important electrical sources of ultraviolet radiation is the exploded wire method of Anderson [27] although it has occasionally been of service in the study of the absorption spectra of vapors. In this method, a fine wire (less than 36-gauge), 5 cm. in length, of nickel, iron, manganese or copper, is fused or exploded by discharging through it a heavy current by means of a large condenser charged by a 500-watt, 26,000-volt transformer, suitably rectified. In series with the wire is an adjustable spark-gap. In air, the method yields a nearly continuous spectrum, with many dark lines, due to absorption by the hot metal vapor.

[19] For other data on the emission of tungsten filaments, see von Alphen, H. C., *Ann. Physik*, **85**, 1058 (1928) and Hoffmann, F., and Willenberg, H., *Physik. Z.*, **35**, 713 (1934).
[20] Borstler, E. W., U. S. P. 1,800,277, April 14, 1931.
[21] For a general discussion, see Lohse, H. W., *Can. J. Research*, **12**, 519 (1935), and Lundegård, H., *Lantbruks-Högskol Ann.*, **3**, 49 (1936).
[22] Lockyer, Sir N., and Austen, R., *Proc. Roy. Soc.*, **23**, 344 (1875); Liveing, G. D., and Dewar, J., *ibid.*, **28**, 352 (1879); Hartley, W. N., *Phil. Trans.*, **185A**, 161, 1047 (1894).
[23] Hemsalech, G. A., and de Watteville, C., *Compt. rend.*, **149**, 1112, 1369 (1909); de Gramont, A., *ibid.*, **157**, 477 (1918); **176**, 1104 (1923).
[24] Wulf, T., *Ann. Physik*, **9**, 946 (1902).
[25] Greinacher, H., *Z. Physik*, **47**, 344 (1928).
[26] Cohn, W. M., *Z. Physik*, **70**, 662, 667, 679 (1931).
[27] Anderson, J. A., *Astrophys. J*, **51**, 37 (1920).

In place of wires, asbestos fibers may be used upon which solutions of the various alkaline-earth chlorides to be analyzed have been evaporated.[28]

A very brilliant light (up to 14,000,000 candles) of extremely short duration (less than 5 millionths of a second) is said to be produced by the explosion in argon of 0.4 cc. of a liquid explosive, such as tetranitromethane. Its spectrum extends far into the ultraviolet.[29]

Electrodeless Discharge. The high-frequency electrodeless discharge has been but rarely employed for carrying out photochemical reactions. Since its discovery by Hittorf in 1884, there has been much discussion as to whether the phenomenon is to be ascribed to an electrostatic or an electromagnetic field.[30]

Apparently either can excite a gas or vapor at low pressure to emit a brilliant diffuse discharge. In these methods, the oscillatory discharge from a condenser goes through a coil of wire surrounding but not touching the reaction vessel. At higher gas pressures, the discharge alters in character and assumes a ring form, the lines changing from a mixture of arc and spark lines to a spectrum in which spark lines predominate. Harkins [31] used a coil of six turns of copper wire around a quartz or "Pyrex" flask with a side-tube arranged for the collection of the products formed during the passage of the discharge through various organic gases. A window was arranged for spectrographic observations of the products transiently produced. The frequency of the circuit was 800 kilocycles per second. The circuit included a 1 k.v.a. Thordardsen transformer which supplied a maximum of 25 kilovolts, a spark gap of cylindrical zinc electrodes adjustable by a screw, and a 0.025 microfarad condenser. In the discharge, both benzene and acetylene were found to be dissociated, giving spectrographic evidence of the presence of H, C, C^+, C_2 and CH. Polymerization led to compounds of very high molecular weights which appeared as solid, reddish-brown flakes. At a pressure of 0.02 mm., 5000 liters of benzene vapor were passed into the flask without changing the character of the discharge; from one to two grams of solid products were formed per hour.

Another type of apparatus [32] is that in which rare gases, especially krypton and xenon, in a vessel at low pressure are subjected to an electric current or electromagnetic field of high intensity by a high-frequency coil. It has a quartz window for ultraviolet irradiation processes so disposed as to be practically outside the high-frequency field. The rare gases emit a gamut of rays from the visible to the very short ultraviolet of value in therapy. The surrounding solenoid is placed far enough from the window so that the latter does not become very hot, permitting the application of the source very close to the part of the body to be irradiated. This lessens the loss of short ultraviolet rays by absorption by the air. The ends of the solenoid wire are joined to a high-frequency apparatus, such as a spark-gap diathermy apparatus. In the discharge in neon, the current density is important, as neon at high current densities emits intensely between 3350 and 3700A.[33] At current densities greater than three amperes per square centimeter, the source emits a spark spectrum, high frequency not being required.

[28] Sawyer, R. A., and Becker, A. L., *Astrophys. J.*, **57**, 98 (1923).

[29] Michel-Lévy, A., and Maurarour, H., *Compt. rend.*, **200**, 543 (1935).

[30] Stuhlman, O., Jr., and Whitaker, M. D., *Rev. Sci. Instruments*, **1**, 772 (1930); Rayleigh, Lord, *Proc. Roy. Soc.*, **150A**, 34 (1935). For the construction of light sources of this sort in the laboratory, see Winans, J. G., *Rev. Sci. Instruments*, **9**, 203 (1938).

[31] Harkins, W. D., *Trans. Faraday Soc.*, **30**, 221 (1934).

[32] French P. 743,167, March 25, 1933, to Soc. anon. pour les Applications des Gaz Rares à la lumière, procédés George Claude; British P. 385,835, Jan. 5, 1933; *Brit. Chem. Abs.* **B**, *1933*, 197; *Chem. Abs.*, **27**, 3671 (1933). Goude-Axelos, J., and Claude, A., *Compt. rend.*, **194**, 132 (1932).

[33] Soc. anon. pour les Applications des Gaz Rares établissements Claude-Paz and Silva, British P. 404,271, Jan. 8, 1934.

The sparking potential in electrodeless discharge tubes diminishes when the tube is illuminated by ultraviolet or visible light.[34]

Radiations produced in metal vapors by the passage of radiations from another source or those furnished by active nitrogen or hydrogen, although theoretically important, do not at present constitute practical sources of ultraviolet radiations.

[34] Zouckermann, R., *Compt. rend.*, **206**, 331 (1938).

Chapter 4

The Spark as a Source of Ultraviolet

The electric spark is rather infrequently used as a source of ultraviolet radiations for effecting photochemical reactions, although it has been employed in some of the more important investigations. The electric spark finds its chief application as a source of a many-lined spectrum suitable for studying absorption spectra of compounds possessing broad absorption bands. (See also Chapter 9.) It is also widely employed as a means of exciting to emission materials to be analyzed by spectrographic methods. Sparks passed in vacuum have yielded information of importance in the region of the extreme ultraviolet. The high tension disruptive electric spark between iron terminals is very rich in ultraviolet radiation and is useful in producing fluorescent effects, particularly in mineral and drug analyses. It is, however, seldom used for this purpose.

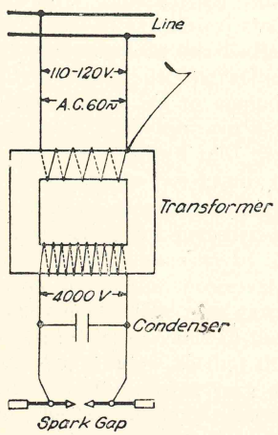


FIGURE 5.

Diagram of Connection, Iron Spark Apparatus.

(Courtesy General Electric Co.)

Iron electrodes were used in a spark outfit designed by Andrews.[1] The connections of the apparatus are shown in Figure 5. A small transformer steps up a 60-cycle, 110-120 volt, alternating current to about 4000 volts. A condenser is connected in series with the iron terminals. The spark gap is adjustable. Assembled apparatus is shown in Figures 6 and 7. As this apparatus uses only about 250 to 300 watts, it can be safely connected to any alternating current lighting circuit.

Ross [2] recommended the use of aluminum terminals, which yielded an intensity of ultraviolet radiation (measured by the liberation of iodine from potassium iodide) twice as great as that resulting when terminals of any other common

[1] Andrews, W. S., *General Electric Rev.*, April, 1916, 319.
[2] Ross, W. H., *J. Am. Chem. Soc.*, **18**, 786 (1906).

metals were used. Cadmium was not recommended because of its softness. The terminals were 3 mm. × 8 mm. in cross-section and were placed 7 cm. apart on iron plates. Small dishes, containing ice and resting on the metal, served to conduct away the heat rapidly.

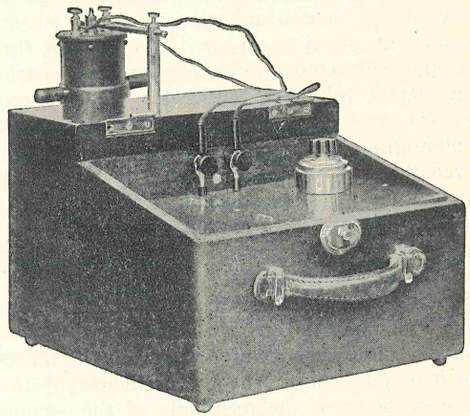


FIGURE 6.

Rear View of "Iron Spark" Apparatus.

(Courtesy General Electric Co.)

ELECTRICAL CIRCUITS EMPLOYED FOR THE PRODUCTION OF SPARKS

When a small potential difference is impressed upon two parallel electrodes separated by an air space, a very small current will be carried across the gap by the few ions present in the air as a result of cosmic rays, radioactivity, etc. As the potential difference is increased, the current increases in accordance with Ohm's law but only so long as the potential difference remains small. With further increases, the current increases less and less rapidly and finally becomes constant (saturation value) over a wide range of impressed potential differences.

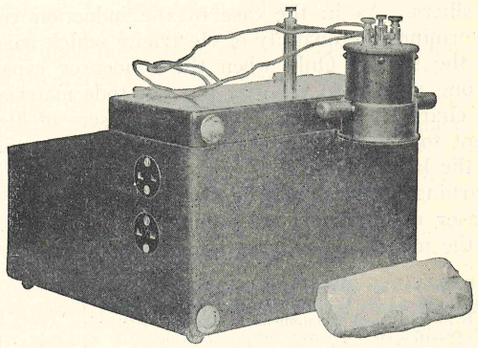


FIGURE 7.

Front View, Portable "Iron Spark" Apparatus.

(Courtesy General Electric Co.)

This occurs because the electrons in a dense gas collide with gas molecules before the electrons can acquire sufficient kinetic energy (from the potential field) to ionize the gas. Thus no new carriers of current are produced.

When the potential difference has been raised to several thousands of volts,

ionization by electron impact occurs suddenly and the current rapidly attains high values. There is a brilliant flash, a spark passes across the gap with the production of a high temperature and the potential difference is temporarily obliterated.

The spark is very brief in duration. What happens following it depends on the nature of the external circuit. Under suitable conditions, the air becomes ionized, the resistance drops, and some form of self-maintained discharge ensues. This may take the form of an arc if the heat of the spark has brought the electrodes to a sufficient temperature. To produce sparks across small gaps, gradients of about 30,000 volts per centimeter are required.[3] The earliest workers to study spark spectra [4] used an induction coil to produce the necessary high potentials. By photographic methods, with rapidly moving films, Schuster and Hemsalech [5] showed that the emission of metal lines was due to an oscillating discharge, and that, following a single discharge through the air, which vaporizes the electrode material, the lines form near the electrodes and then cross the gap at rates of 400 to 1300 meters per second. The particles composing the streamers were found to be electrically charged.[6]

Studies with rotating mirrors have shown that a break in the primary circuit of the induction coil causes a series of secondary discharges, the first of these secondary discharges being bright and the others faint. The first is a true spark, since it may be shown (by the oscillograph) to follow upon a very high potential difference between the terminals of the secondary winding. Such a discharge, repeated at each interruption of the primary current, emits a spectrum which is characteristic of the gas through which it passes, and exhibits but a few faint lines from the metal of the electrodes. Early spectroscopists spoke of this spark as "uncondensed," a term now known to be incorrect, since all sparks are associated with a condenser discharge. In this case the condenser was the air-gap itself together with the capacity of the secondary winding. In all sparks, the discharge is oscillatory because of the inertia effect of self-induction in the winding. Most workers, however, employed a condenser (in parallel with the spark gap) charged by the induction coil to the necessary sparking potential. (Figure 5.)

The induction coil may be replaced by a small high tension alternating current transformer, thus eliminating difficulties arising in the operation of contact-breakers. As in the case of the induction coil, the capacity of the condenser determines the quantity of electricity which passes in each spark and the intensity of the spark. Only when the condenser capacity is sufficient is the discharge strong enough to vaporize the electrode material into the discharge, there to emit its characteristic lines. With condensers of high capacities, the intensity is sufficient to ionize the atoms of the electrode metal and produce the spark spectrum of the latter. The sizes of transformer and condenser must be so chosen that the sparking potential may be obtained or exceeded. Details of transformer and condenser requirements are found in a paper by Anderson [7] and in the publications of the makers of spectrographic equipment.

[3] For further detailed discussions of spark theory, see Loeb, L. B., *Rev. Modern Phys.*, **8**, 267 (1936); Rogoski, W., *Z. Physik*, **100**, 1 (1936); Pirani, M., *Angew. Chem.*, **44**, 395 (1931); Darrow, K. K., "Electrical Phenomena in Gases," Baltimore, Williams and Wilkins, 1932.

[4] Hartley, W. N., *Phil. Trans. Roy. Soc.*, I, 50 (1884); II, 327; Pollok, J. H., and Leonard, A. G., *Proc. Roy. Soc. Dublin*, **11**, No. 16, 17, 18 (1907); No. 23, 24 (1908); No. 31 (1909).

[5] Schuster, A., and Hemsalech, J. G., *Phil. Trans.*, **193A**, 189 (1900).

[6] Milner, S. R., *Phil. Trans.*, **209**, 71, 1908; see also Royds, T., *Ibid.*, **208**, 333 (1908); *Phil. Mag.*, **19**, 285 (1910). Their velocities have been measured recently. Miyanishi, M., *Japan. J. Phys.*, **5**, 67 (1928); *Chem. Abs.*, **23**, 4404 (1929); Asami, Y., *Elec. Eng. Japan*, **53**, 27 (1933); *Chem. Abs.*, **27**, 2630 (1933); Toriyama, Y., and Shinohara, U., *Elec. Eng. Japan*, **53**, 100 (1933); *Chem. Abs.*, **27**, 2630 (1933).

[7] Anderson, J. A., *Astrophys. J.*, **59**, 76 (1924).

A high capacity condenser causes slower oscillations in the discharge, thereby increasing the amount of electricity secured in each oscillation. This prolongs the train of sparks and produces a heating effect on the electrodes. de Kowalsky [8] showed that the region of maximum radiated energy is displaced toward the longer wave-lengths as the oscillatory current is increased. Increasing the amount of energy consumed in the spark, however, causes displacement in the opposite direction, although this is to some extent dependent upon the nature of the electrodes. The intensity of the mean ultraviolet radiation emitted varies inversely with the frequency.

The oscillations may also be made slower by introducing additional self-inductance, the rate of oscillation varying inversely as the square root of both the capacity and self-inductance of the circuit. A self-inductance coil, called frequently a Hemsalech coil,[9] has the property of making the "air-lines" disappear, the spectrum being then largely from the electrodes. The self-inductance coil is introduced in series with the gap at A in Figure 8.

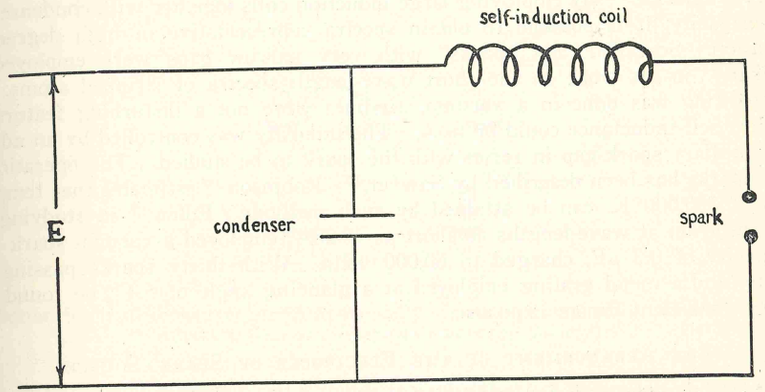


FIGURE 8. Diagram of Spark Circuit. (Twyman and Smith, "Wavelength Tables for Spectrum Analysis" London, Adam Hilger Ltd.).

The form of the discharge depends upon the amount of self-inductance employed since the latter decreases the rate of oscillations, and also lessens the current which passes in the first discharge, spreading the current more evenly over a series of oscillations. Without any self-induction, the oscillations are strongly damped by the resistance of the gap, so that most of the energy passes in the first spark. With self-induction, less current passes during the first spark and the oscillations continue for a longer time.

In the first case (no self-induction), the first strong spark is believed to excite the gas and to send some vaporized metal from the electrodes. The discharge then dies away rapidly and the metal vapor cools. Subsequent oscillations are too weak to vaporize more metal. With but little metal vapor in the gap, the resistance and potential are high and the electrons acquire sufficient kinetic energy to excite the gas. With self-inductance the first spark is not strong enough to excite the gas and its lines are not evident. The cumulative effect of the subsequent discharges is, however, sufficient to heat and vaporize the metal. The introduction of this

[8] de Kowalsky, J., *Compt. rend.*, **158**, 1337 (1914); *Bull. Soc. Int. Elect.*, **4**, 437.

[9] Hemsalech, J. A., *Compt. rend.*, **122**, 285 (1899); Schenck, C. C., *Astrophys. J.*, **14**, 116 (1901); *Phil. Trans.*, **193A**, 189 (1900).

heated metal vapor into the gap lowers the resistance and the potential and the electrons fail to acquire sufficient energy to excite the gas. As the metal becomes ionized when the spark carries enough current, all of the arc lines are present. The prolongation of the oscillations under these conditions led de Gramont to speak of such sparks as oscillating sparks as distinguished from the condition which he called the "condensed" spark. This is misleading for both are oscillatory and condensed in fact.[10]

The effects of variations in capacity and self-inductance are particularly important when the spark is employed as a source for the spectrographic analysis of metals. Since spectrographic analysis involves technique which requires considerable experience and since this subject does not fall within the province of this book, further details must be sought in manuals devoted to spectrographic essays. For spectrographic analysis, Scheibe and Neuhäusser recommended[11] 0.0033 mfd. capacity and 0.000015 henry of self-induction. Resonance transformers[12] and high frequency transformers have been recommended.[13]

"Hot Sparks." By employing large induction coils together with condensers of high capacity, it is possible to obtain spectra representative of high degrees of ionization. So-called "hot sparks" with very narrow gaps were employed by Millikan[14] in his work on the short wave-length spectra of stripped atoms. As the sparking was done in a vacuum, air-lines were not a disturbing feature, so that low self-inductance could be used. The intensity was controlled by an adjustable auxiliary spark-gap in series with the spark to be studied. The operation of these sparks has been described by Sawyer.[15] Robinson[16] estimates that temperatures of 300,000°K. can be attained by such methods. Edlén[17] in studying the C V spectrum at wave-lengths as short as 40.28A, employed a vacuum spark with a capacity of 0.3 μF, charged to 60,000 volts. With thirty sparks passing per minute, and a metal grating employed at a glancing angle of 5.4°, he found half an hour sufficient for an exposure.

The Arrangement of the Electrodes of Spark Sources

In studying the emission spectra of metals or alloys, it is necessary to support two blunt-pointed rods or heavy wires of the material so that a gap is formed. Adjustable supports for the rods are desirable. The spectra of minerals can be obtained by attaching them to rods by spring clips.[18]

Boas[19] passes a high speed current of air past the spark in order to destroy the aureole surrounding it. He also describes an electrostatic relay to maintain a constant distance between the electrodes. The latter erode rapidly if thin. On

[10] See also Negresco, T., *J. Chim. Phys.*, **25**, 308 (1928).

[11] Scheibe, G., and Neuhäusser, A., *Angew. Chem.*, 1218 (1928); see also Meggers, W. F., Kiess, C. C., and Stimson, F. J., *Bureau of Standards Sci. Paper No. 444*, 1922; Sweitzer, E., *Z. anorg. allgem. Chem.*, **164**, 127 (1927); Kosbahn, T., *Ann. Physik*, **25**, 625 (1936); Gibbs, R. C., Vieweg, A., and Gaertlein, C. W., *Phys. Rev.*, **34**, 406 (1929); Langstroth, G. O., and McRae, D. R., *Canadian J. Research*, **16A**, 17, 61 (1938).

[12] Boas, H., *Z. Physik*, **60**, 690 (1930).

[13] Hull, F. A., and Steele, G. J., *Proc. Am. Soc. Testing Materials*, **27**, II (1927); Gerlach, W., and Schweitzer, E., *Z. anorg. allgem. Chem.*, **195**, 255 (1931); Potopenko, G., *Ibid.*, **215**, 44 (1933); Goroncy and Urban, Ibid., **211**, 28 (1933); Feussner, O., *Z. Metalkunde*, **25**, 73 (1933).

[14] Millikan, R. A., *Astrophys. J.*, **52**, 47 (1921); **53**, 150 (1921); *Phys. Rev.*, **12**, 168 (1918); *Science*, **19**, 138 (1919).

[15] Sawyer, R. A., *Astrophys. J.*, **52**, 286 (1920); Sawyer, R. A., and Smith, F. R., *J. Opt. Soc. Am.*, **14**, 287 (1927).

[16] Robinson, H. A., *Z. Physik*, **100**, 636 (1936).

[17] Edlén, B., *Nature*, **127**, 405 (1931).

[18] Heraeus, W. C., G.m.b.H., British P. 400,607, Oct. 18, 1933.

[19] Boas, H., *Z. Physik*, **60**, 690 (1930).

the other hand the spark may move from place to place on a thick electrode. Gring and Clark[20] described a stand capable of holding four pairs of electrodes, any pair of which can be quickly brought into position for exposure.

Arrangement of Electrodes. Spark sources have been employed in measuring the extent of some photochemical reactions. In such cases, uniformity over a prolonged time is necessary. Forbes and Brackett secure this by striking the spark[21] between adjacent edges of two square bars of metal (see Figure 9). The latter

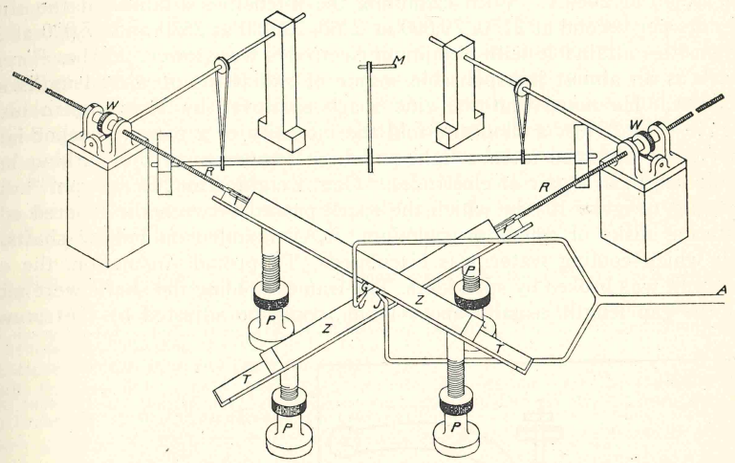


FIGURE 9. Spark Source for Automatically Constant Illumination (Forbes and Brackett, *Journal American Chemical Society*).

move in horizontal planes at right angles to each other. Conduction and radiation of heat are so rapid that erosion is at a minimum. The method avoids hand control required by previous workers with sparks and monochromators.[22] In the apparatus, flexible woven metallic bands connect two $400 \times 25 \times 25$ mm. bars to a condenser. The bars rest in rectangular troughs perpendicular at right angles. Posts P are insulated from the base board by vulcanite blocks. The upper trough is cut away at G to expose the lower edge of the upper bar. The ends of the troughs are raised or lowered by turning the milled heads until the bars are horizontal, and their separation along the common diagonal is 2 mm. The shortest path for the spark lies along this one line. Blasts of air provided by two vacuum cleaners in tandem converge from the jets J upon the gap at G to blow back the corona. A ventilated housing conducts away oxide fumes. Threaded rods R, ending in insulating links I, pass through sleeves rotated by worm gears W, retracting the bars. The optimum speed varies with the energy of the spark and the volatility of the metal. Zinc bars, operated at 250 mm. per hour, give 1½ hours net service for each of the four pairs of edges. When a pair of edges has been used up, the current is interrupted, the oxide crusts detached, the threaded rods

[20] Gring, J. L., and Clark, G. L., *Rev. Sci. Instruments*, **7**, 305 (1936).

[21] Forbes, G. S., and Brackett, F. P., Jr., *J. Am. Chem. Soc.*, **53**, 3973 (1931).

[22] Warburg, E., *Sitzb. Preuss. Akad. Wiss.*, 746 (1911); Beckman, A. O., and Dickinson, R. G., *J. Am. Chem. Soc.*, **52**, 124 (1930).

returned to their original positions, and operation is started with a fresh pair of edges. The depth of erosion on the upper edge is constant at 1.2 mm. for zinc and 0.5 mm. for aluminum. On the lower edge, it is about two-thirds as much. A 5 kv. oil transformer is operated at 110 volts and 35 amperes under control of a voltage regulator. The gap voltage is 6500 ± 500, secured by employing a heavy duty mica condenser of 0.04 microfarad capacity.

With the monochromator employed, it was possible to secure approximately monochromatic radiations in the case of zinc of 30,000 ergs per second at 2530A, and of 16,000 at 2080A. With cadmium, the intensities attained at the slit were 34,000 ergs per second at 2170, 79,000 at 2260, 22,000 at 2570 and 27,000 at 2710A. The intensities attainable with aluminum electrodes were lower. Forbes [23] regarded the spark as an almost indispensable source of radiations of wave-lengths shorter than 2500A. He noted that the zinc spark employed by Warburg in his early work gave [24] at 2540A a thousand-fold the intensity of a mercury vapor lamp.

Lifschitz [25] obtained intense light and high temperatures by sparking between the whole length of a pair of electrodes. Ogg, Leighton and Bergstrom [26] describe a spark gap (Figure 10) in which the spark passed between the tapered edges of two rotating disks of cobalt or cadmium, A,A′ mounted on hollow shafts, B,B′, through which cooling water was circulated. To provide insulation, the cooling water circuit was broken by sprinklers. The frames holding the shafts were movable, so that the gap length, usually about 1 cm., could be adjusted by the screws I,I′.

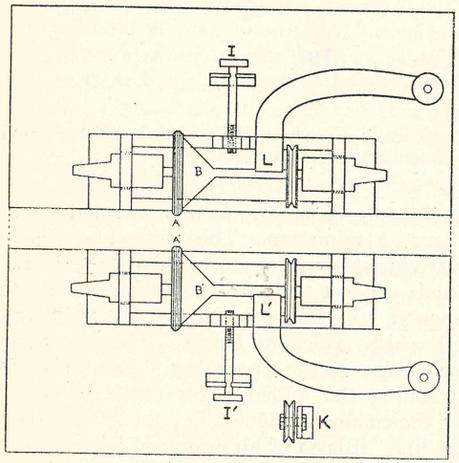


FIGURE 10.

Spark Gap with Rotating Water-cooled Electrodes (Ogg, Leighton and Bergstrom, *Journal American Chemical Society*).

The shafts were belt-driven in opposite directions at several hundred r.p.m. by a ¼ h.p. motor. Electrical contact was made through heavy carbon brushes L,L′, connected to the terminals of a 0.010 mfd. oil-immersed condenser across the secondary of a 5 kw. x-ray transformer. By this means one to two discharges per half cycle were obtained across the gap. A hose (attached to a vacuum line)

[23] Forbes, G. S., *J. Phys. Chem.*, **32,** 485 (1928).
[24] Warburg, E., *Sitzb. Preuss. Akad. Wiss.*, 746 (1911); 216 (1912); 314 (1916).
[25] Lifschitz, S., German P. 524,877, March 26, 1926; *Chem. Abs.*, **25,** 4189 (1931).
[26] Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **55,** 1754 (1933). See also van der Lingen, J. S., *S. African J. Sci.*, **33,** 197 (1937).

mounted close behind the spark drew off objectionable fumes. The gap was readily demountable for cleaning and oiling of the bearing and interchange of electrode disks.[27]

Photochemical Reactions in Gases Surrounding Sparks

Jolibois, Lefebvre and Montagne [28] state, from observations on the change in pressure, that carbon dioxide at pressures between 0.3 and 20 mm. of mercury when subjected to a spark discharge, is decomposed into carbon monoxide and oxygen. A limiting dissociation of 90 per cent is attained. About 20 per cent of the energy of the first spark is converted into chemical energy; the remainder is dissipated. The decomposition increases with the voltage and is influenced by the size and shape of the containing vessel and the position of the electrodes. The yield rises to a maximum and falls as the capacity of the circuit decreases, and for a given capacity the maximum yield falls off slightly as the pressure increases.

Methane, under a pressure of 1 to 11 mm., was transformed into ethylene and hydrogen [29] under a spark discharge. Apparently little industrial use has been made of the radiations from a spark gap, although its use as a means of generating a bleaching gas for flour and cornmeal has been patented.[30]

[27] For other spark apparati, see Henri, V., *Compt. rend.*, **157,** 126 (1913); Kuhn, W., *Ibid.*, **178,** 708 (1924).
[28] Jolibois, P., Lefebvre. H., and Montagne, P., *Compt. rend.*, **182,** 1026 (1926); **184,** 522 (1927). General discussions are due to Lefebvre, H., *Chimie et Industrie,* Special Number, June, 427, 1933, and to Jolibois, P., *Ber.*, **71A,** 73 (1938).
[29] Montagne, P., *Compt. rend.*, **194,** 1490 (1932).
[30] Stuff, F., German P. 510,419, Dec. 23, 1927; *Chem. Abs.*, **25,** 1008 (1931); German P. 518,201, June 28, 1929; *Chem. Abs.*, **25,** 2377 (1931); German P. 521,360, Dec. 25, 1929; *Chem. Abs.*, **25,** 2651 (1931); Brabender, C. W., *Mehlprobleme,* **1,** 6 (1932).

Chapter 5

The Open Arc

Arcs may be produced between electrodes that are open to the air or enclosed in a vessel of glass or quartz. In the case of the enclosed arcs, the pressure may be very low or it may be atmospheric or greater.

In most arcs, the use of very high starting potentials is obviated by bringing the electrodes into contact (closed circuit) and then drawing them apart. The resistance offered to the passage of the current heats the electrodes to a temperature such that, when drawn apart, they produce vapors of the electrode material. The latter carry a bright discharge across the intervening space. The arc discharge, which may carry many amperes, is very hot and the electrodes become brightly luminous.

The mechanical features of the arc vary with the use for which it is intended, as commercial illumination, spectrographic analysis, as an ultraviolet source for conducting photochemical reactions or for fluorescence studies. An arc which will emit ultraviolet energy strongly may be prepared by employing an iron rod and a carbon rod for the two poles. Also, two iron rods may be used. These poles are cooled by means of heavy brass or copper sleeves, which may be moved along the iron rods as the latter are consumed. Thus, the upper pole (negative) may be an iron rod about one-quarter inch in diameter. This rod is surrounded by a movable but well-fitted sleeve of copper about one inch in diameter with hollowed end. One pole should be adjusted vertically. In preparing the arc, a bead of molten metal is developed in the dished end of the lower electrode. The upper electrode is well cooled and the arc is maintained very steadily between the bead of molten iron and the upper solid electrode. Luckiesh has had such an arc operate at a rather high current density for thirty minutes without any adjustment.

Electrical Characteristics

Metallic arcs in general will not burn on alternating current. The carbon (but not the graphite) arc will, however, burn on alternating currents at potentials as low as 80 volts. On direct current, the carbon arc burns with voltages as low as 37. Iron and copper arcs require higher voltages, 80 and 90 at least. Arcs between electrodes of materials with good thermal conductivity tend to extinguish readily.

A number of observers have developed empirical equations for the relation between the length of the arc and the voltage, or between the energy, current, voltage and arc length.[1] The Ayrton equation for the carbon arc, $V = A + B/I$, has been made more accurate and more general by Nottingham by raising the current I to a power n. A and B are constants depending upon the arc length

[1] Ayrton, Mrs. H., "The Electric Arc," Chapter IV, New York, van Nostrand, 1902; Malcolm, H. W., and Simon, H. T., *Physik. Z.*, **8**, 471 (1907); Steinmetz, C. P., *Trans. Am. Inst. Elec. Eng.*, 802 (1906); Bramhall, E. H., *Phil. Mag.*, **13**, 682 (1932); Nottingham, W. B., *Am. Inst. Elec. Eng.*, **42**, 12 (1923); *Phys. Rev.*, **28**, 764 (1926); Anderson, S. H., and Kretchmar, G. A., *Phys. Rev.*, **26**, 33 (1925); Doan, G. F., and Myer, J. L., *Elec. Eng.*, Sept., 1932; Sommer, J. J., and Bott, J., *Physik. Z.*, **34**, 324 (1933); Kotecki, A., *Acta Phys. Polon.*, **4**, 113 (1935).

and pressure. The equation applies if the anode is very hot. The power n is a constant dependent upon the boiling or sublimation point of the metal of the anode. It is 0.67 for copper, 1.38 for tungsten, and approximately 1 for carbon, the latter accounting for the success of the Ayrton equation. The dependence of this constant upon the nature of the anode led Myer [2] to suggest that the anode may have a more important role in the arc mechanism than most theories of the arc discharge would imply. Alterthum and Ewest [3] believe that the anode exerts an important effect over the entire discharge, for by preheating the anode, the striking and operating voltage of the arc can be greatly reduced. Hagenbach and Langbein [4] stated that in normal arcs, the anode is boiling during discharge. The form of the equation also shows that an increase in the current is accompanied by a drop in the potential, showing that Ohm's law does not apply to conduction in the arc.

With heavy currents, above ten amperes, the voltage approaches the limiting value A. The pressure of the gas is also a factor. The required potential increases continuously with the pressure; the values at ten atmospheres may be 15 to 20 volts greater than at one atmosphere.[5]

The theory of the mechanism of the arc discharge has lagged somewhat behind practice. The development of the quartz mercury-vapor arc was based to a large extent upon empirical observations and trial and error methods. The theory of the open arc is still the subject of many controversial statements.[6] The development of arc theory may be approached through a consideration of the phenomena of glow discharge at low pressures, which has been summarized by Dushman,[7] Langmuir,[8] and by Pirani.[9]

The various easily recognizable regions of the glow discharge are also found in arcs through gases at low pressures but are masked in the high-pressure or open arc. The theories of the latter are, however, based upon the application of principles derived from the study of the glow discharge. The fundamental processes of the emission of electrons from hot cathodes, the liberation of electrons by thermal ionization of atoms and molecules of gases, the acceleration of electrons in potential fields and the results of impact of electrons with atoms and molecules leading to excitation and the emission of radiations, all are encountered in high-pressure or open arcs as they are in the glow discharge. Complications in study of open arcs arise from such effects as the high temperature glow of the electrodes, vaporization and sputtering of the electrodes and combustion in the flame of the arc.

Thermionic emission of electrons from the cathode, heated by positive ion bombardment, has been believed adequate to account for the current densities in the tungsten arc or carbon arc.[10] Although the temperatures of the copper, iron and

[2] Myer, J. L., *Trans. Am. Inst. Elec. Eng.*, **52**, 250 (1933).

[3] Alterthum, H., and Ewest, H., *Z. tech. Physik*, **9**, 221 (1928).

[4] Hagenbach, A., and Langbein, K., *Arch. Sci.*, **1**, 48 (1919).

[5] See also Anderson, S. H., *Phys. Rev.*, **29**, 750 (1927).

[6] For a detailed earlier account, see Compton, K. T., *J. Am. Inst. Elec. Eng.*, **46**, 868, 1192 (1927).

[7] Dushman, S., *Elec. Eng.*, **53**, 1204, 1283 (1934).

[8] Langmuir, I., *Gen. Electric Rev.*, **38**, 514 (1935).

[9] Pirani, M., *Z. angew. Chem.*, **44**, 395 (1931); Lex, E., Pirani, M., and Rompe, R., *Naturwiss.*, **23**, 393 (1935). See also for greater details, Langmuir, I., and Compton, K. T., *Rev. Mod. Physics*, **3**, 191 (1931); Found, C. G., and Forney, J. D., *J. Am. Inst. Elec. Eng.*, **47**, 747, 855 (1928); Kirschstein, B., and Koppelmann, F., *Z. tech. Physik.*, **15**, 604 (1934), and the books, Kohler, W., and Rompe, R., "Die Elektrischen Leuchtrohre," Vieweg, 1933; Seeliger, R., "Physik der Gasentladungen," Leipzig, Barth, 1927; Darrow, K. K., "Electrical Phenomena in Gases," Baltimore, Williams and Wilkins, 1932.

[10] Nottingham, W. B., *J. Frank. Inst.*, **205**, 811 (1928); Mason, R. C., *Phys. Rev.*, **38**, 427 (1931).

nickel arc cathodes have been found to lie near the boiling points of these metals [11] such temperatures are said to be too low to produce sufficient electrons to give the observed current densities.[12] Furthermore, so-called "cold cathode" arcs are known to be obtainable.[13] Slepian reported that the arc current to the cathode may be carried by positive ions resulting from thermal ionization of the gas, in accordance with the Saha equation. The necessary temperatures of 6000 to 7000° were assumed to exist in a thin layer of gas next to the cathode. Langmuir [14] introduced a different theory in which electrons are assumed to be drawn from the cathode by a very intense electrostatic field near the cathode surface set up by a positive space-charge sheath, a view further developed by Mackeown and Compton.[15]

Much work has been done upon the relation between the potential drop at the cathode and the ionization potentials of the gases or vapors which emit radiations when the molecules or atoms are struck by the electrons. Electron densities have also been related to the intensities of lines or bands emitted.[16] Nottingham states the cathode drop of 20 volts in the copper arc to correspond with the second ionization potential of copper vapor. In the cadmium arc, the drop, 8.4 volts, agrees with the ionization potential of cadmium. In the thallium arc, the drop was slightly higher than 6.08 volts, the ionization potential of thallium. In the carbon arc, the cathode fall of 5 volts agreed fairly well with the ionization potential (4.4 volts) of the cyanogen molecule. It may be noted, however, that others report the cathode drop of the carbon arc as 9 volts. That the electrons in the arc plasma could have the necessary velocities to give the required excitation energies implies that the electrons must have a greater velocity of agitation than might be expected from the potential gradient between collisions. The velocity of agitation of the electrons implies an "electron temperature." By the use of the Langmuir probe methods, Nottingham [17] found this temperature to be 6000° for the cadmium arc, 8000° for the thallium arc and 19,000° for the copper arc, or sufficient to account for the observed intensities of the emitted lines.[18]

In the course of his work on arc temperatures, Nottingham [19] developed a photographic method for finding the area of the hot spot on the cathode from which the arc passes. This area appeared to increase in proportion to the total current, so that the current density remained constant. In the arc itself, a magnetic field due to the current tends to concentrate the discharge about a longitudinal axis in its center.[20]

The vapors distilled from metallic arcs have been studied by Rayleigh [21] and by Berkey and Mason.[22] Matter is lost from the cathode of an iron arc. The decrease in weight of the latter is not proportional to the current alone, but depends

[11] Hagenbach, A., and Langbein, K., *Arch. Gen.*, **461**, 329 (1918); Tanberg, R., and Berkey, W. E., *Phys. Rev.*, **38**, 296 (1931).

[12] Slepian, J., *Phys. Rev.*, **27**, 407 (1926); Seeliger, R., *Physik. Z.*, **27**, 22 (1926); **31**, 691 (1930).

[13] Nicol, J., *Proc. Roy. Soc.*, **82A**, 29 (1909); Stolt, H., *Z. Physik*, **26**, 95 (1924).

[14] Langmuir, I., *Gen. Elec. Rev.*, **26**, 735 (1923); *Z. Physik*, **46**, 282 (1927).

[15] Mackeown, S. S., and Compton, K. T., *J. Am. Inst. Elec. Eng.*, **46**, 1192 (1927). See, however, Slepian, J., and Haverstick, E. J., *Phys. Rev.*, **33**, 52 (1929), and Mason, R. C., *Ibid.*, **38**, 427 (1931).

[16] See for the copper arc measurements, Bramhall, E. H., *Phil. Mag.*, **13**, 682 (1932); Ornstein, L. S., and Vermeulen, D., *Z. Physik*, **70**, 564 (1931); Schmidt, R. W., *Z. Physik*, **106**, 35 (1937); Robertson, R. M., *Phys. Rev.*, **53**, 578 (1938).

[17] Nottingham, W. B., *J. Frank. Inst.*, **206**, July, 1928; **207**, March, 1929; **208**, 192 (1929).

[18] See, however, Bramhall, E. H., *Phil. Mag.*, **13**, 682 (1932). These relations have been discussed more exactly in the positive columns of low pressure gas discharges.

[19] Nottingham, W. B., *J. Frank. Inst.*, **205**, 811 (1928).

[20] Northrup, E. F., *Phys. Rev.*, **24**, 474 (1907).

[21] Rayleigh, Lord, *Proc. Roy. Soc.*, **112A**, 14 (1926).

[22] Berkey, W. E., and Mason, R. C., *Phys. Rev.*, **38**, 943, 1783 (1931).

also upon the cooling of the cathode.[23] The whole surface adjacent to the bright spot contributes to the loss. This vaporization of the electrodes makes their nature of particular importance in determining the potential difference across an arc of given length, and in obtaining the constants in the modified Ayrton equation. The transport of luminous material in the arc has been studied by measuring the variations in the intensities of the spectral lines in different portions of the arc,[24] as well as by other methods.[25] Very high velocities have been observed.[26]

Spectrographic Arcs [26a]

An arc between iron electrodes generally is employed in spectroscopy. Baly [27] used a horizontal arc with the iron poles mechanically rotated in opposite directions. The arc was stated to be capable of giving long exposures. This was a modification of a device of Crew and Tatnall [28] in which one electrode comprised a rapidly revolving disk mounted on the armature of a motor and carrying on its periphery small pieces of the metal whose spectrum was to be observed. The other electrode was a rod of the same metal mounted on a fine-cut screw so that the position of the electrode could be accurately adjusted.[29]

The Pfund arc,[30] used as a steady source for the measurements of wave-lengths of the iron arc, is vertically mounted. In operation, the iron arc makes a transition from a high voltage stage to a low voltage stage with currents of about one ampere. Cady and Arnold [31] find the excess potential in the high voltage stage to lie in the anode fall. The iron arc burns at low voltages in impure argon, helium or neon, but cannot be struck in these gases if the latter are rigidly purified.[32]

An enclosed iron arc described as a convenient source for the standardization of spectral lines [33] emits a discharge in an inert gas. The latter is maintained at atmospheric pressure. In this manner one electrode is heated to a temperature sufficient to provide enough metal vapor to yield the iron spectrum. At least one electrode is compacted of sintered pure iron or iron compounds and contains an electron-emitting substance such as barium or calcium oxide. Titanium, tungsten, molybdenum and chromium must be absent to prevent confusion in reading the spectrum. A window for transmitting the radiations is placed on a tubular extension of the bulb.

Data on exact wave-lengths of the standard lines of the iron arc have been

[23] Schmick, H., and Seeliger, R., *Physik. Z.*, **29**, 864 (1928). See also Laudet, G., *Compt. rend.*, **192**, 202 (1931), and Kirschstein, B., *Wiss. Veröffent. Siemens-Werken*, **16**, 69, 72 (1937); *Chem. Abs.*, **31**, 7341 (1937); **32**, 2034 (1938).

[24] Ornstein, L. S., and Koopmans, T., *Proc. Acad. Sci. Amsterdam*, **34**, 1099 (1931); *Chem. Abs.*, **26**, 4755 (1932).

[25] Tanberg, R., *Phys. Rev.*, **35**, 1080 (1930).

[26] See, e.g., Slepian, J., and Mason, R. C., *Phys. Rev.*, **37**, 779 (1931); Compton, K. T., *Ibid.*, **36**, 706 (1930).

[26a] For a summary of recent theory, Rollwagen, *Spectrochem. Acta*, **1**, 66 (1939).

[27] Baly, E. C. C., "Spectroscopy," Vol. **2**, p. 91, London, Longmans Green and Co., 1927.

[28] Crew, H., and Tatnall, R., *Phil. Mag.*, **38**, 379 (1894).

[29] See also Neuhaus, C. J., *Am. Soc. Testing Materials*, Preprint No. 51 (1938); *Chem. Abs.*, **32**, 6105 (1938).

[30] Pfund, A. H., *Astrophys. J.*, **27**, 296 (1908).

[31] Cady, W. G., and Arnold, H. D., *Physik. Z.*, **8**, 890 (1907).

[32] Doan, G. E., and Myer, J. L., *Phys. Rev.*, **40**, 36 (1932).

[33] British P. 401,509, Nov. 16, 1933 (Patent-Treuhand Gesellschaft für elektrische Glühlampen, assigned to General Electric Co., Ltd.); see also Pirani, M., and Rompe, R., *Z. tech. Physik*, **13**, 134 (1932).

reported by Babcock [34] and by Burns and Walters,[35] with particular reference to the vacuum arc.*

Ultraviolet Sources for Photochemical Processes

Temperatures and energies emitted in small tungsten arcs have been studied by de Groot.[38] Moore [39] employs electrodes of an alloy composed essentially of tungsten with 1-5 per cent of titanium and 0.25-2.0 per cent of chromium. The tungsten arc between rods of 6.4 mm. diameter is rather unsteady and hard to keep in focus because of the formation of a crust of oxide around the electrode. It is weak in rays of less than 2300A, from which wave-length there is a gradual increase in intensity to a maximum at 4500A.

Arcs carrying 6 amperes between 12 mm. nickel rods are said to provide quiet-burning sources of ultraviolet, emitting strongly at 2300 and at 3500A.[40] Macdonald [41] produces ultraviolet rays by means of an arc created in a vacuum from electrodes of gold alloyed with copper or silver. Nagaoka and Suguira [42] described an arc in which the cathode was a carbon rod coated with barium or strontium oxide, the rod being sheathed in a silica tube. Various metals or salts in a similar silica tube served as anode. The arc operated in a vacuum and at 1500 volts produced rays which penetrated aluminum foil. Vaporization of the anode metal, short life of the arc, and the necessity of cooling the system and pumping to maintain vacuum were among the reported disadvantages of this arc. Albers [43] described an apparatus for maintaining an enclosed beryllium arc in any atmosphere at reduced or elevated pressures.

The Carbon Arc

The carbon arc was discovered by Sir Humphry Davy, between 1802 and 1808. He employed a 2000-plate voltaic battery as source of current and obtained an arc three inches long. The development of carbon arcs has followed two chief paths. One is the design of steady, very brilliant arcs for motion-picture projection or for air-port illumination. The second has been concerned with methods for altering the distribution of the intensity of the radiation within various spectral regions to meet special demands of industrial photochemistry. Also, the carbon arc is utilized for therapeutic purposes. Much of the progress has been due to alterations in the carbon electrodes.

An early advance consisted in the introduction of a central core of a soft, neutral composition, which stabilizes the arc stream and prevents the latter from shifting

* What is known as the pole-effect is a slight difference in the wave-lengths of many lines when the arc is examined near the poles or at the center.[36] The pole-effect does not affect ordinary analytical methods and is of importance only in precise spectrographic work. In some instances, revolving electrodes may be employed.[37]

[34] Babcock, H. D., *Astrophys. J.*, **67**, 240 (1928).

[35] Burns, K., and Walters, F. M., Jr., *Pub. Allegheny Observatory*, **6**, 159 (1929); *Chem. Abs.*, **23**, 4886 (1929).

[36] St. John, C. E., and Babcock, H. D., *Astrophys. J.*, **42**, 231 (1915).

[37] Sventitskii, N. S., *Zavodskaya Lab.*, **6**, 325 (1937); *Chem. Abs.*, **31**, 7762 (1937).

[38] de Groot, W., *Physica*, **5**, 121, 234 (1925); *Chem. Abs.*, **19**, 2449, 3215 (1925). For line measurements, see Laun, D. D., *Phys. Rev.*, **48**, 572 (1935).

[39] Moore, W. G., U. S. P. 1,872,322, Aug. 16, 1932; *Chem. Abs.*, **26**, 5857 (1932). Note also Blake, G. G., British P., 279,680, Jan. 4, 1927.

[40] Coblentz, W. W., Dorcas, M., and Hughes, C. W., *Sci. Papers, Bureau of Standards*, **21**, No. 539, p. 547 (1926).

[41] Macdonald, R. F., British P. 206,588, Aug. 9, 1922; *Chem. Abs.*, **18**, 1090 (1924).

[42] Nagaoka, H., and Suguira, Y., *Astrophys. J.*, **57**, 86 (1923).

[43] Albers, V. M., *J. Opt. Soc. Am.*, **19**, 146 (1929).

about the rim of the crater. Coating the carbons with copper or other metals lessens overheating. The light from either the solid or the neutral-cored carbon arc (on direct current) comes almost entirely from the crater of the positive carbon, little being derived from the arc stream or the tip of the negative carbon. With alternating current, there are two craters of light, but the brilliancy and efficiency are somewhat less than that secured with direct current.

There have been developments in the application of refractory coatings. Thus, the electrodes may be placed in a silica tube and heated to 700° in a current of silicon tetrafluoride at a pressure slightly above atmospheric to form a non-oxidizable coating which retards combustion.[44] Other coatings of silicon or tungsten carbides [45] or of sprayed chromium on the carbon [46] have been described. In some instances, the carbon first is covered with silvered copper, and the whole sprayed with chromium. The use of a cellulose lacquer coating to prevent the absorption of water on the carbon, which causes flickering, has been proposed by Wilson.[47] As the arc passes, the positive terminal becomes hollowed out to a crater, while the negative terminal remains pointed. According to Griffith, Taylor and Jack [48] the flame of the arc contributes most of the radiation which is effective therapeutically. The efficiency of the arc increases to a limiting value with flame length, above which the efficiency is independent of flame length. The ultraviolet emission is a function of the watts consumed in the flame of the arc.

A high intensity carbon arc, intended for motion picture projection in large theatres, comprises cored $\frac{9}{16}$ mm. positive carbons (without metallic coatings) and smaller copper-coated negative carbons.[49] The arc is operated with a horizontal positive carbon, continuously rotated to maintain a well-formed crater. The cathode is placed at an angle 40-60° below the horizontal. Arc currents of 60 to 190 amperes are employed at 45 to 90 volts, d.c. The spectral energy distribution is said to be similar to that of sunlight. The crater furnishes 70 per cent of the light, the remainder coming from the tail-flame. The color and brilliancy of the light indicate a temperature of 5500°C. Since this is higher than the vaporization temperature of carbon, the source must be other than the solid tip of incandescent carbon. Alternating current high intensity arcs have been developed. High intensity carbons usually are cored with cerium fluoride or some similar material. The very high current densities require the use of oxides, fluorides, etc., in a central rod, embedded in the carbon.[50] Only difficultly vaporizable substances may be used in the core. Alkalies must be avoided as they are detrimental to the brilliancy of the crater.[51] Beck has described the construction of a negative electrode for high intensity arcs.[52]

Temperatures in the arc may be estimated by a study of the intensities of band

[44] Singleton, W., and Hare, A., British P. 248,167, March 17, 1925 (General Electric Co., Ltd.).

[45] I. G. Farbenindustrie, German P. 578,501, June 14, 1933.

[46] C. H. Champion and Co., Ltd., and Champion, C. H., British P. 406,434, March 1, 1934.

[47] Wilson, W. N., British P. 395,073, July 13, 1933.

[48] Griffith, H. D., Taylor, J. S., and Jack, J. M., *Brit. J. Radiology*, **23**, 203 (1927); *Chem. Abs.*, **21**, 3830 (1927).

[49] Kalb, W. C., *Elec. Eng.*, **53**, 1173 (1934); **56**, 319 (1937). See also Bassett, P. R., *Trans. Am. Electrochem. Soc.*, **44**, 153 (1923). The toxicity of the fumes from such arcs appears to be due primarily to nitric oxide, carbon monoxide being negligible, according to MacQuiddy, E. L., Tollman, J. P., LaTowsky, L. W., and Bayliss, M., *J. Ind. Hyg. Toxicol.*, **20**, 297, 312 (1938); Coltman, R. W., *Ibid.*, **20**, 289 (1938).

[50] Orne, S. W., U. S. P. 1,867,524, July 12, 1932; *Chem. Abs.*, **26**, 4544 (1932); Dorcas, M., U. S. P. 1,920,921, Aug. 1, 1933; *Chem. Abs.*, **27**, 4746 (1933).

[51] British P. 285,424, June 19, 1929 (Compagnie Lorraine de Charbons pour l'Electricité); see also U. S. P. 1,952,810, March 27, 1934; *Chem. Abs.*, **28**, 3317 (1934), and British P. 475,252, Nov. 16, 1937; *Chem. Abs.*, **32**, 3280 (1938).

[52] Beck, H., U. S. P. 1,991,998, Feb. 19, 1935.

spectra.[53] Ornstein and Brinkman [54] concluded from the intensity of the cyanogen bands at 3884 and 4216A, that the violet kernel of the carbon arc shows a temperature of 6500°K. Lower temperatures of 2950 to 3600° were obtained when the bands of AlO were produced by filling the anode cup with alumina and carbon. Other results indicated the arc gases to have temperatures exceeding those of the electrodes, showing that the high temperature of the gas plays an essential role in the discharge mechanism.[55] By a method based upon the reflectivity of carbon, Warmuth [56] calculates the temperature of the positive crater to be 3740°C. Chaney, Hamister and Glass [57] find the temperature of the positive crater to approach as a limit the sublimation point of pure crystalline graphite. They state the maximum brightness temperature of the carbon crater is probably 3810°K or 40° higher than that found by Waidner and Burgess. The true crater temperature they believe to be between 3925 and 3970°K.

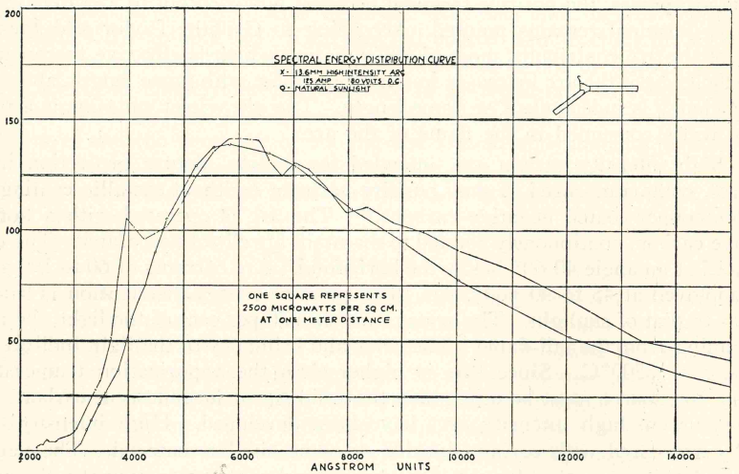


FIGURE 11. Spectral Energy Distribution Curves of Sunlight and High-intensity Carbon Arc (Greider, *Industrial and Engineering Chemistry*).

Ryde [58] found that in arcs with a positive carbon cored with calcium fluoride and operated at current densities greater than the limiting current densities for ordinary carbons, a bright central core develops in the arc stream. In the central core, the spectra of neutral carbon, nitrogen and oxygen, the Balmer series of

[53] v. Engel, A., and Steenbeck, M., [*Naturwiss.*, **19**, 212 (1931); *Chem. Abs.*, **25**, 2357 (1931)], use the absorption of x-rays.

[54] Ornstein, L. S., and Brinkman, H., *Naturwiss.*, **19**, 462 (1931); *Proc. Acad. Sci. Amsterdam*, **34**, 33, 498 (1931); *Chem. Abs.*, **25**, 3567, 5842 (1931).

[55] Ornstein, L. S., Brinkman, H., and Vermeulen, D., *Proc. Amsterdam*, **34**, 764 (1931); Ornstein, L. S., *Physik. Z.*, **32**, 517 (1931); Ornstein, L. S., Brinkman, H., and Beunes, A., *Z. Physik*, **77**, 72 (1932); Mason, R. C., *Physica*, **5**, 777 (1938); *Chem. Abs.*, **32**, 8364 (1938). For determinations by other methods see Hörmann, H., *Z. Physik*, **97**, 539 (1935). Lochte-Holtgreven, W., and Maecker, H., [*Z. Physik*, **105**, 1 (1937)] raise the values from cyanogen bands to 7600° for the normal and to as high as 8700° for an over-run arc. See also Khlebnikova, L. Y., *J. Exptl. Theor. Phys. (U.S.S.R.)*, **7**, 1220 (1937); *Chem. Abs.*, **33**, 4866 (1939); Khramova, E. F., *J. Exptl. Theor. Phys. (U.S.S.R.)*, **8**, 176 (1938); *Chem. Abs.*, **33**, 4866 (1939).

[56] Warmuth, K., *Wiss. Veröffentlich. Siemens-Konz.*, **7**, 307 (1928); *Chem. Abs.*, **23**, 316 (1929).

[57] Chaney, N. K., Hamister, V. C., and Glass, S. W., *Trans. Electrochem. Soc.*, **67**, 107 (1935).

[58] Ryde, J. W., *Proc. Roy. Soc. London*, **117A**, 164 (1927).

hydrogen and some argon lines are excited. Of the two chief band systems, *i.e.*, the Swan bands and the cyanogen bands, the former are strongly excited close to and inside the positive carbon, but do not appear at all in the arc stream under normal conditions. The origin of the cyanogen bands is well established, since they are absent when the arc is operated in a gas free from nitrogen. The Swan bands appear to be formed by C_2.[59] An increase in current rapidly increases the intensity of the cyanogen bands.

The distribution of energy in the carbon arc operated under various conditions has been determined by Greider,[60] who employed a quartz monochromator for the region between 2300 and 7000A and an infrared spectroradiometer between 6000 and 18000A. The relative energy distribution curves were converted into absolute energy unit curves by a method involving the use of a galvanometer and thermopile.[61] In the curves reproduced in Figures 11 and 12, unit areas represent unit amounts of energy, so that the intensity between any two wave-length limits may be estimated by measuring the corresponding area under the curve.

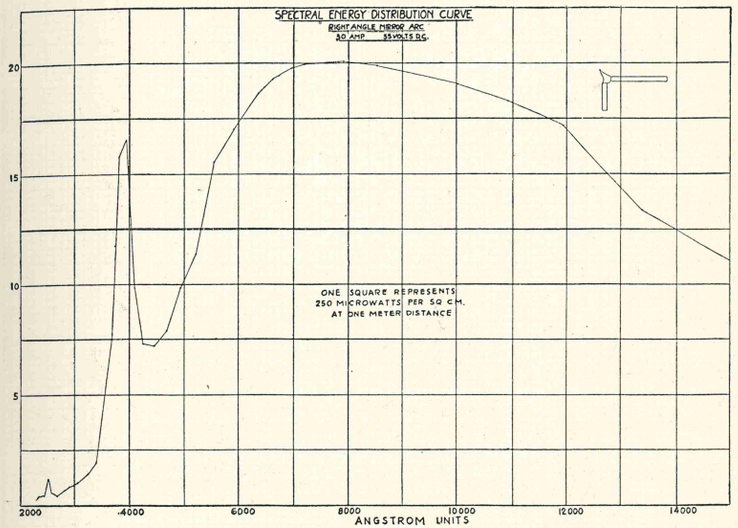


FIGURE 12. Spectral Energy Distribution Curves of Plain-carbon Arc, Burned under Low-intensity Conditions (Greider, *Industrial and Engineering Chemistry*).

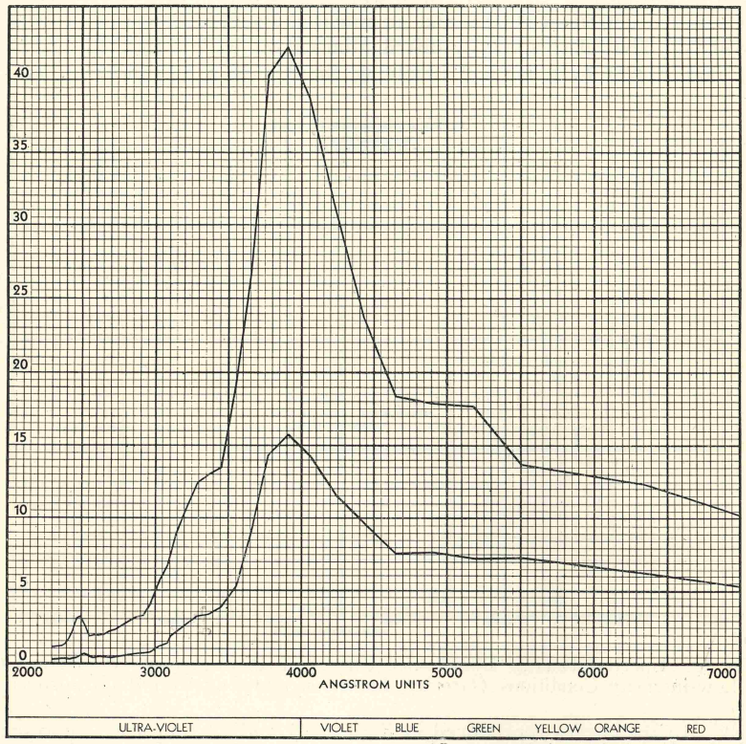
Figure 11 compares the energy distribution from a 13.6 mm. high-intensity arc operated at 125 amperes and 80 volts d.c. with that of normal sunlight. Each square represents 2500 microwatts per sq. cm. at a distance of one meter. The agreement is quite remarkable, the chief difference being in the greater output by the arc of radiations shorter than about 4500A. The spectrum also extends to a shorter wave-length limit, although this forms but an insignificant fraction of the total radiation from the arc.

[59] Johnson, R. C., *Nature*, **116**, 539 (1925); Johnson, R. C., and Asundi, R. K., *Proc. Roy. Soc., London*, **124A**, 668 (1929).

[60] Greider, C. E., *Ind. Eng. Chem.*, **23**, 508 (1931); for a discussion of the methods employed in such measurements, see Chapter 7.

[61] Greider, C. E., and Downes, A. C., *Trans. Illum. Eng. Soc.*, **25**, 378 (1930); **27**, 637 (1932). See also Mandel'shtam, S. L., *Compt. rend. acad. sci. U.R.S.S.*, **18**, 559 (1938).

The energy distribution of the plain carbon arc with poles at right angles and carrying 30 amperes at 55 volts is shown in Figure 12 in which each square represents but one-tenth of the energy of the previous figure. This arc burns at a lower temperature, so that the total intensity is lower, and the intensity maximum occurs at a longer wave-length. There appears also a larger amount of the line or band spectrum from the arc stream, giving peaks at 2500 and 3900A. When a plain vertical carbon arc is utilized, there is found to be relatively less continuous radiation from the craters. Also the maximum intensity lies much farther toward



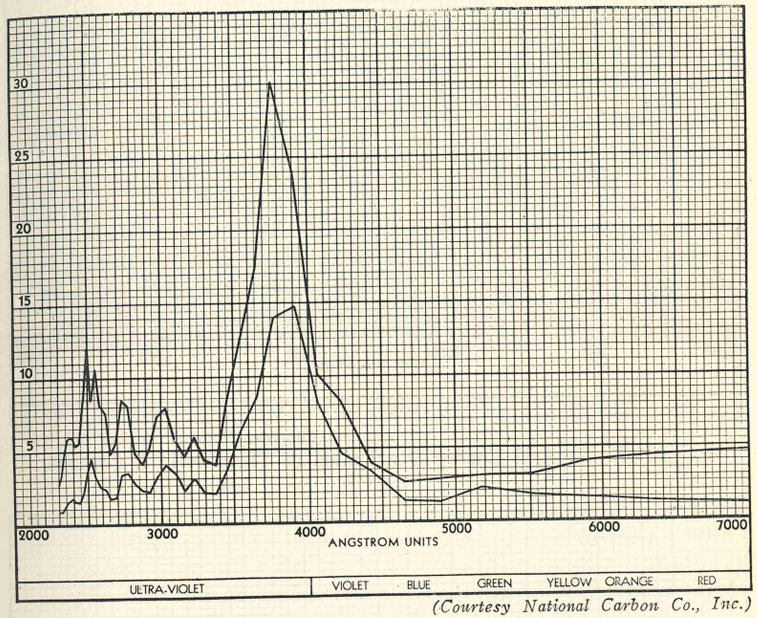
(Courtesy National Carbon Co., Inc.)

FIGURE 13. Spectral Energy Distribution of Sunshine Carbons.

the infrared than with high intensity carbons. This flame carbon arc may be made into a versatile source of radiation by the addition to the electrode of various substances, which may be vaporized into the arc. The added materials are either distributed throughout the carbon or, more commonly, are concentrated into a central core.

Figure 13 gives the energy distribution of Sunshine carbons which contain cerium in the core. As compared with the neutral core arc, there is a marked increase of energy in the ultraviolet, increasing gradually in intensity from about 2900 to 4000A. There is a fairly uniform intensity at a much lower level, from about 4500 to 8000A, due to lines so closely packed together as to yield a nearly continuous spectrum. Beyond about 8000A the intensity falls off rapidly, practically

all radiation in this area being that from the incandescent poles. Such arcs are especially suitable for photography and photoengraving. Reactions believed to occur within the arc stream or hot electrodes of the cerium carbons have been discussed by Bassett.[62] These carbons are also suitable for therapeutic arcs in which it is desired to imitate sunlight. The lower and upper curves in Figure 13 refer to the output of the arcs operated with 30 and 60 amperes, respectively. Figures 14, 15, 16, 17, and 18 give similar data for various other therapeutic carbons ("B," "C," "E," "K" and "U" are the trade designations). In each case the output increases much more rapidly than the rate of current increase. Up to about 30 amperes, the output is approximately equal to the square of the current, but at higher currents the rate of output decreases. The "B" carbons contain iron and yield light similar in general distribution to that of the mercury arc.

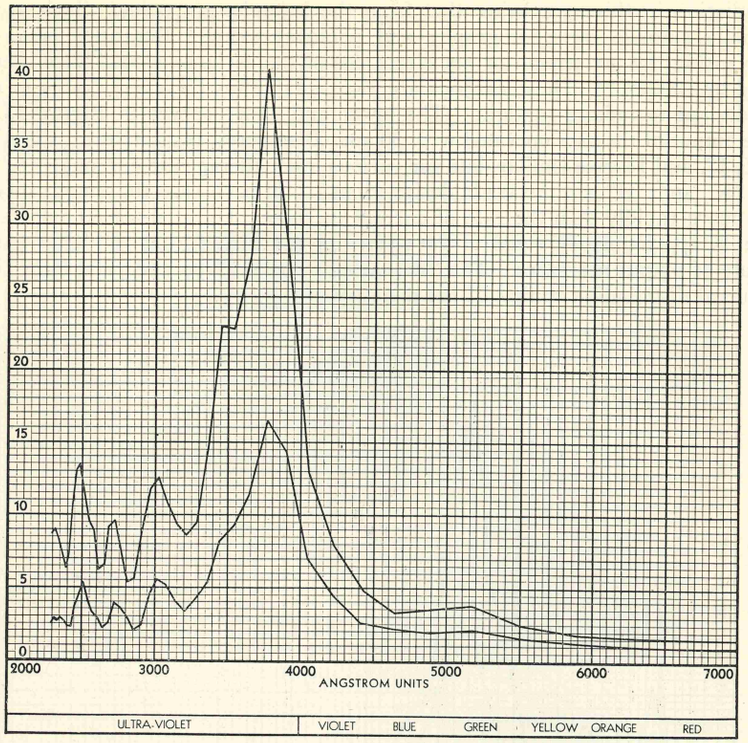


(Courtesy National Carbon Co., Inc.)

FIGURE 14. Spectral Energy Distribution of Therapeutic B Carbons.

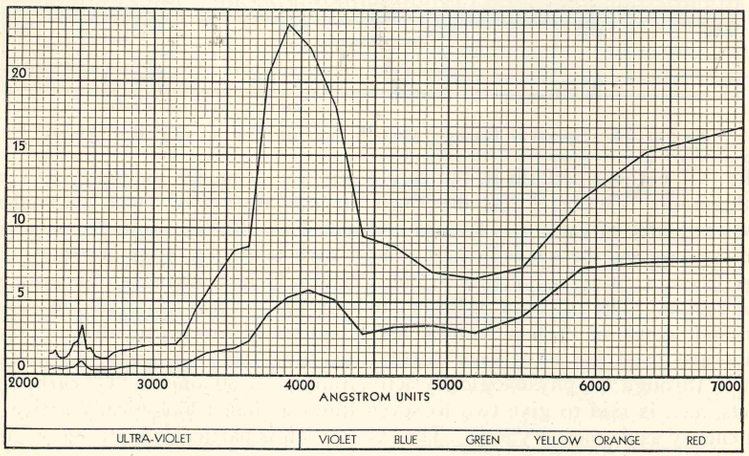
The "C" carbons contain in the core a mixture of metals including iron, nickel and aluminum. Dorcas[63] has described the preparation of these electrodes. A hollow shell tube of carbon is formed and baked at 1400°C. Into the tube is then forced the core and the whole heated. These carbons give a series of groups of very intense lines in the ultraviolet, with but a relatively low intensity of energy in the visible region. The infrared radiation follows the general shape of the curve for the incandescence of carbon craters, but is relatively low in intensity. The "C" carbons are used for ultraviolet therapy as they have an even distribution of radiation through the physiologically active range. A 30-ampere "C" carbon arc at 50 volts, a.c., is said to give two to seven times as much biologically active ultraviolet energy as do mercury arcs. The "C" carbon is particularly strong in the zone

[62] Bassett, P. R., *Trans. Electrochem. Soc.*, **44**, 153 (1923).
[63] Dorcas, M. J., U. S. P. 1,862,300, June 7, 1932.



(Courtesy National Carbon Co., Inc.)

FIGURE 15. Spectral Energy Distribution of Therapeutic C Carbons.

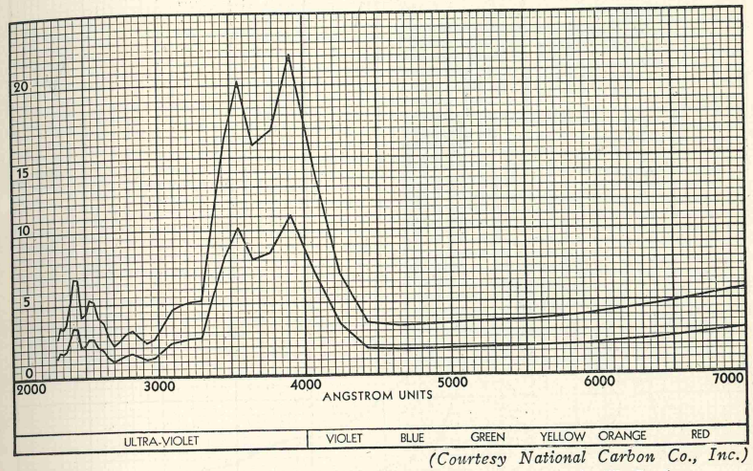


(Courtesy National Carbon Co., Inc.)

FIGURE 16. Spectral Energy Distribution of Therapeutic E Carbons.

of antirachitic radiation (2700 to 3000A) and is the strongest of all therapeutic carbons of the National Carbon Co. series in the tan-producing zone from 3000 to 3200A.

To secure particular energy distributions in the ultraviolet wires of zinc or aluminum may be embedded in holes bored in the carbon. Copper and cobalt usually are added in powder form to the carbon. Cobalt ("K" carbons) gives a very high intensity near 2400A and a peak near 3600A, with a low intensity in the visible and infrared in comparison with the plain carbon arc. In absolute units the energy is not far different at 9000A and at the 2400A peak. This carbon is said to simulate in effects the Kromayer mercury arc. (See page 126.)



(Courtesy National Carbon Co., Inc.)

FIGURE 17. Spectral Energy Distribution of Therapeutic K Carbons.

To secure particularly the region 2800 to 3100A, Greider [64] employs about equal quantities of iron, chromium, manganese and titanium in the core of the carbon. Arcs with calcium or strontium compounds in the core have relatively little energy in the ultraviolet. The strontium arc ("E" carbons) is used in infrared therapy. The intrinsic brilliance of the flame of all these arcs is relatively low, but the size of the flame is stated to give volume and efficiency.[65]

The effects of various proportions of iron in the anode on the spectrum of the carbon arc have been determined by Reiniers.[66] With 30 to 90 per cent of iron, the cyanogen band could still be detected, but most of the other bands disappeared when 2 per cent of iron was present, with the exception of those at 5152-5159A. The latter can still be detected with 25 per cent iron in the carbon.

Peczalski [67] has shown that the spectrum of the internal layers of an arc salted with calcium fluoride consists principally of calcium fluoride bands.[68] Reiter and

[64] Greider, C. E., U. S. P. 1,920,255, Aug. 1, 1933 (to National Carbon Co.). See, however, O'Brien, B., U. S. P. 2,121,882, June 28 1938; *Chem. Abs.* **32,** 6353 (1938).

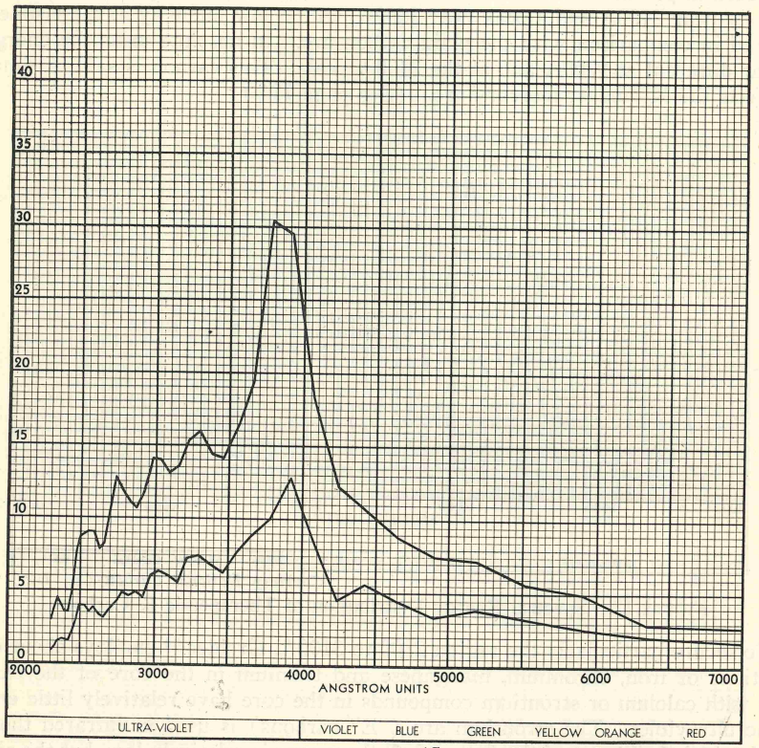
[65] Extensive studies of the emission of various carbons have also been made at the Bureau of Standards. Coblentz, W. W., Dorcas, M. J., and Hughes, C. W., *Sci. Papers Bureau Standards,* **21,** No. 539 (1926); Coblentz, W. W., *Am. J. Electrotherapeutics and Radiology,* **63,** 455 (1925).

[66] Reiniers, J. H., Jr., *Verslag Akad. Wetenschappen Amsterdam,* **33,** 655 (1924); *Chem. Abs.,* **19,** 2300 (1925).

[67] Peczalski, T., *Compt. rend.,* **199,** 405 (1934); Szulc, N., *Ibid.,* **201,** 48 (1935).

[68] For details of the preparation of carbon electrodes containing calcium fluoride, see M. and V. Arnone, British P. 247,831, Feb. 25, 1926; *Chem. Abs.,* **21,** 536 (1927); and also Orne, S. W., U. S. P. 1,867,524, July 12, 1932; Canadian P. 310,628, April 21, 1931.

Gabor [69] describe an arc in which at least one electrode containing silver is used in conjunction with various filters. This arc was stated to produce a strong spectrum between 3300 and 3600A, lines of wave-lengths less than 3200A being practically absent. The arc was intended for use in the stimulation of plant growth. (See, however, Chapter 44.)



(Courtesy National Carbon Co., Inc.)

FIGURE 18. Spectral Energy Distribution of Therapeutic U Carbons.

For therapeutic radiations, Chesney [70] employs carbon with iron carbide and at least two ferroalloys of metals, such as uranium, tungsten, vanadium, molybdenum, yttrium, titanium, tantalum and zirconium, having complementary spectra rich in ultraviolet. E. and O. Conradty [71] add bismuth or a salt of bismuth to the core of a carbon arc.

Lavoisier [72] uses as one electrode a dehydrated and glazed mixture of zirconia and yttria. Volmer [73] uses electrodes of metal oxides, nitrides, carbides or silicates.

[69] Reiter, T., and Gabor, D., U. S. P. 1,856,969, May 3, 1932 (to Siemens and Halske, A.-G.); *Chem. Abs.*, **26**, 3447 (1932).

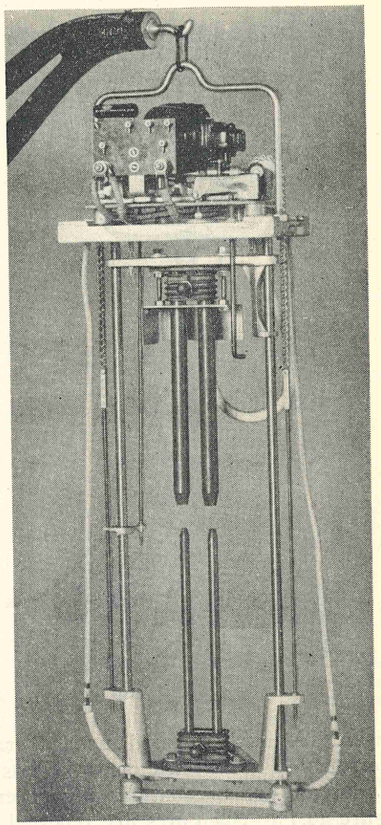
[70] Chesney, J., U. S. P. 1,838,741, Dec. 29, 1931 (to U. V. Generator Corp.); *Chem. Abs.*, **26**, 1202 (1932).

[71] Conradty, E., and Conradty, O., French P. 710,913, Feb. 6, 1931; *Chem. Abs.*, **26**, 1526 (1932).

[72] Lavoisier, I. J., U. S. P. 1,682,847, Sept. 4, 1928 (to Burdick Corp.); *Chem. Abs.*, **22**, 3848 (1928).

[73] Volmer, M., British P. 418,988, Oct. 29, 1934; U. S. P. 2,074,600; *Chem. Abs.*, **29**, 2454 (1931).

The metals suggested include zirconium, magnesium or aluminum with the addition of ferric oxide. Moore and Hole [74] use powdered tungsten sintered with iron and titanium and add other metals to supply radiations in any desired part of the spectrum.



(Courtesy National Carbon Co., Inc.)

FIGURE 19.
Industrial Carbon Arc.

Unusual designs of carbon arcs have been proposed. Pauthenier [75] used a rotating arc and Pierucci [76] employed an electrolyte as one electrode of an alternating current carbon arc. Rocard and de Rothschild [77] direct gas currents along the electrodes. According to Gauthier, Le Bozec and Dubois,[78] a cathode for rotary flame arcs comprises a hollow annular ring in which a cooling liquid flows con-

[74] Moore, W. G., and Hole, K. W., British P. 450,552, July 20, 1936; Moore, W. G., British P. 245,872; *Chem. Abs.*, **21**, 363 (1927).

[75] Pauthenier, *Compt. rend.*, **180**, 1834 (1925).

[76] Pierucci, M., *Nuovo cimento*, **12**, 1 (1935); *Chem. Abs.*, **29**, 3607 (1935).

[77] Rocard, Y. A., and de Rothschild, P., British P. 287,160, March 17, 1927.

[78] Gauthier, G., Le Bozec, L., and Dubois, R., U. S. P. 1,793,605, Feb. 24, 1931; *Chem. Abs.*, **25**, 2061 (1931).

tinuously. An apparatus for producing an electric arc in which a gaseous hydrocarbon is led between two concentric carbon electrodes has been described.[79]

For commercial arcs intended as photochemical sources, some type of automatic feed for one or both of the poles is necessary to keep the arc length constant though the pole materials suffer destruction. In some instances an electromagnetic device is employed which alters the distance between poles as the current through the arc

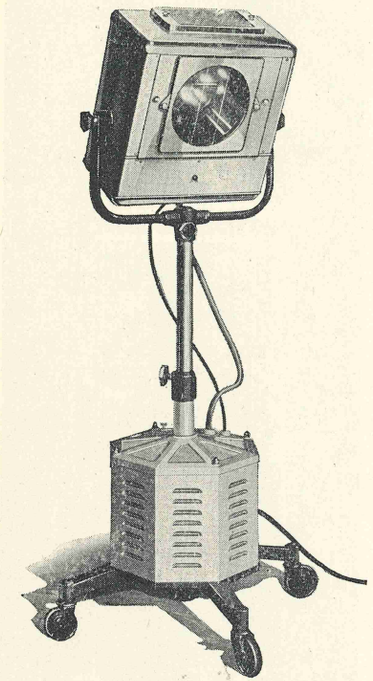


FIGURE 20.

Eveready Model A-2 Carbon Arc Lamp.

(Courtesy National Carbon Co., Inc.)

changes. A method based upon thermostatic control has been advocated by Patterson.[80] Photoelectric control [81] has also been proposed.[82]

Industrial arc installations have been developed by the National Carbon Co. (Figure 19.)[83] Such arcs are reported to operate for ten hours or more without attention, and to be capable of remote or automatic control. It is claimed the ultraviolet shorter than 4000A can be produced by this arc in commercial quantities with a switchboard efficiency of over 12 per cent. A typical medium-sized unit uses 3

[79] Presslicht-Patent-Verwertungsgesellschaft, German P. 579,682, June 29, 1933; *Chem. Abs.*, **28**, 980 (1934).

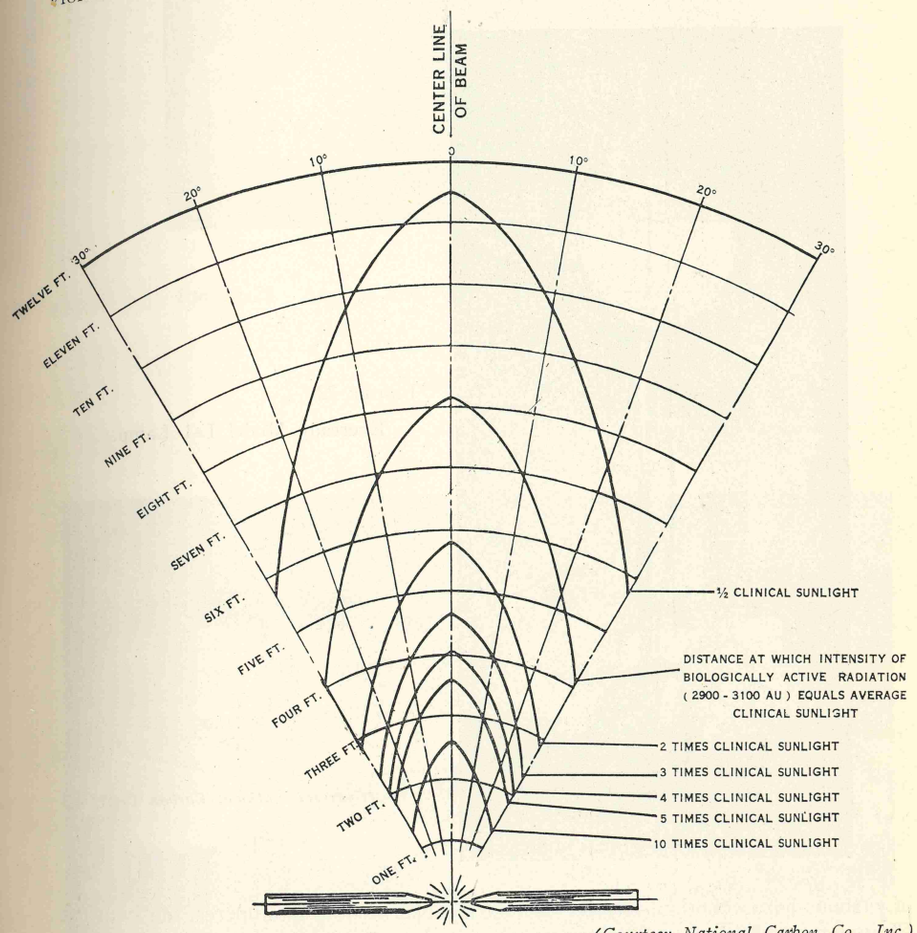
[80] Patterson, M. L., U. S. P. 1,778,770, Oct. 21, 1931; *Chem. Abs.*, **25**, 6 (1931).

[81] Lennox, E. A., British P. 383,853, Nov. 24, 1932.

[82] Other details of mechanical construction and control: Tappan, C., British P. 412,844, July 5, 1934; Boardman, R., British P. 372,552, May 1, 1931; Taylor, A., and Heathcote, R., British P. 416,170, Sept. 13, 1934; Woerner, H. B., U. S. P. 1,705,798, March 19, 1929; Siemens-Schuckert Werke, British P. 390,624, April 13, 1933; Robinson, F. W., British P. 379,524 Sept. 1, 1932; Zeiss Ikon, A.-G., British P. 381,452, Oct. 6, 1932; 414,316, Aug. 2, 1934; 405,597, Feb. 8, 1934; Hall, B. J., British P. 396,876, Aug. 17, 1933; Anderson, N. J., and Rigby, R., Ltd., British P. 391,059, April 20, 1933; Cricks, Rigby and Rigby, Ltd., British P. 400,692, Nov. 2, 1933; Volmer, M., U. S. P. 2,004,680, June 1, 1935; British P. 418,988, Oct. 29, 1934.

[83] Dorcas, M. J., *Ind. Eng. Chem.*, **22**, 1244 (1930).

kilowatts (59 volts, 60 amperes) directly from a 220-volt a.c. line through transformers. With "C" carbons, it would give about 50×10^{-6} watt per square millimeter (at one meter horizontal distance from the arc) of radiation shorter than 6500A. About half of this radiation is in the ultraviolet range. Each square meter (and there are 12.5 such around the arc) can be irradiated with 25 watts of ultraviolet. Such units are of value in the food and stock- and poultry-feed industries.



(Courtesy National Carbon Co., Inc.)

FIGURE 21. Curves of Uniform, High-intensity Sunshine Carbons.

Arc lamps with special housings are available (Figure 20) equipped with a removable Corex D glass filter for lessening the output of radiations shorter than 2900A. The lamp uses 115-volt, 60-cycle alternating current. Figure 21 indicates the intensities of the 2900 to 3100A radiations at various positions with respect to the center of the beam, as compared with their intensities in average sunlight. A simpler form of arc lamp (Figure 22) is also utilized. These lamps may be equipped

with adaptors and applicators for irradiation of small areas. (Figure 23.) Large motor-fed solarium units (one-arc, two-arc and four-arc types) make possible the treatment of from 18 to 20 patients at one time (Figure 24) and are in use in many hospitals, schools and sanatoria. Such units,[84] also adapted to clubs and swimming pools, use carbons 12 feet long. The arc burns between only one pair of carbons at a time, shifting to another set every half hour as the carbons burn back. One trim

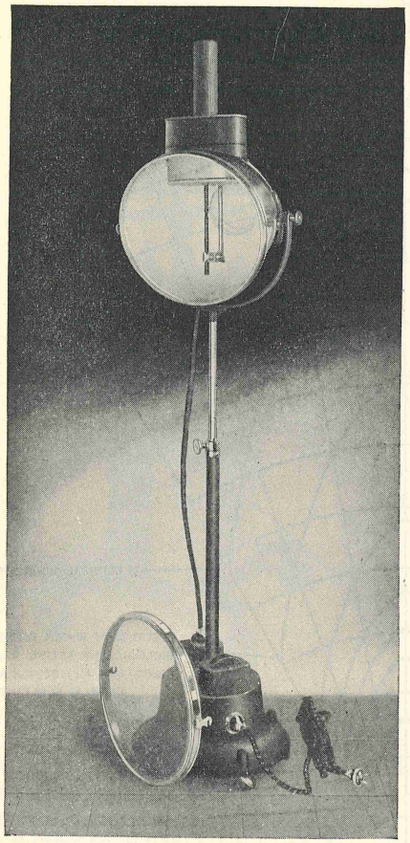


FIGURE 22.
Eveready Model L-1 Lamp.

(Courtesy National Carbon Co., Inc.)

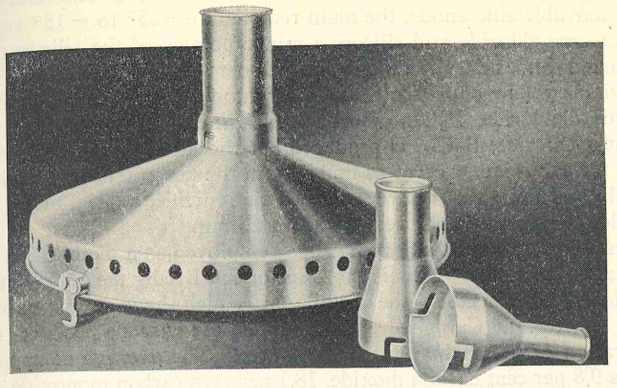
of carbons burns continuously for 12 hours if operated at 45 amperes, ten hours at 60 amperes or 8 hours at 90 amperes.

An arc for splitting hydrocarbon gases to acetylene and hydrogen and for synthesizing hydrogen cyanide has been described.[85] The zinc-graphite arc has been employed under liquids as a reducing agent.[86] Under carbon disulfide, the optimum yield of carbon subsulfide was almost 50 per cent of that represented by the reaction:

[84] Kalb, W. C., *J. Am. Inst. Elec. Eng.*, **49**, 1031 (1930).

[85] Soc. pour l'ind. chim. Bâle, German P. 607,331, Dec. 21, 1934; British P. 389,761. See also Briner, E., Desbaillets, J., and Paillard, H., *Helv. Chim. Acta*, **21**, 115 (1938).

[86] Stock A., Brandt, A., and Fischer, H., *Ber.* **58B**, 643 (1925).



(Courtesy National Carbon Co., Inc.)

FIGURE 23. Adaptor and Applicators for Model L-1 Lamp.

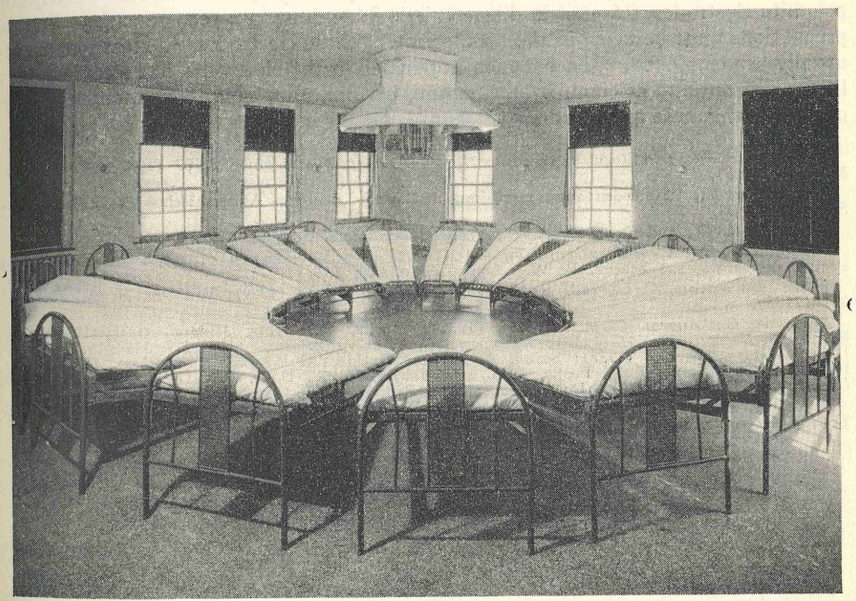


FIGURE 24. Solarium Carbon-Arc Equipment.

$3CS_2 + 4Zn \rightarrow C_3S_2 + 4ZnS$. With silicon tetrachloride, a stationary aluminum cathode and movable zinc anode, the main reaction at $-55°$ to $-15°$ consists in the production of zinc chloride and silicon, a minor portion of the silicon tetrachloride being converted into hexachlorodisilane. Under similar conditions, phosphorus trichloride yields yellow phosphorus and zinc chloride, together with small amounts of phosphorus dichloride, P_2Cl_4. Boron trichloride is converted into boron; to a minor extent a chloride, B_2Cl_4, is produced but the latter was not freed completely from silicon tetrachloride, present as impurity in the boron trichloride used.

Maslowski and Regulski [87] have produced zinc nitride, Zn_3N_2, by an arc between zinc electrodes in nitrogen at a pressure below 25 mm.

Under-water operation of an arc has been employed as a method for disintegrating the electrode materials. This is the basis of the Bredig method for the preparation of colloidal suspensions, the details of which have been summarized by Svedberg.[88] Carter and Campbell [89] have studied the gaseous products formed during the operation of the carbon arc under water. The average composition of the products was 9.8 per cent carbon dioxide, 18.1 per cent carbon monoxide, 3.3 per cent oxygen, 49.3 per cent hydrogen, 3.2 per cent saturated hydrocarbons and 14.6 per cent residual gas, mostly nitrogen. Finely dispersed graphitic acid also was formed.

Plotnikow [90] has described accessory equipment for rendering large and small carbon arcs suitable sources for the demonstration of the phenomena of ultraviolet fluorescence. With suitable filters, carbon arcs can be used as sources of infrared for clinical photography.

The carbon arc may also be employed in spectrographic analysis. The material to be tested may be placed within a hole drilled in the lower carbon electrode. Details of analysis are found in manuals of spectrographic analysis.[91] Acheson graphite electrodes, 0.6 mm. in diameter and 5 cm. long, are recommended. Special precautions must be taken in the purification of these electrodes.[92] Heat treatments usually are employed. The common impurities in the electrodes include vanadium, lithium, strontium, calcium, iron, titanium, barium, aluminum, boron, copper, magnesium, manganese and silicon.[93]

[87] Maslowski, K., and Regulski, H., *Compt. rend. soc. polonaise phys.*, **3**, 87 (1927); *Chem. Abs.*, **23**, 5114 (1929).

[88] Svedberg, T., "Methoden zur Herstellung Kolloider Lösungen Anorganischer Stoffe," Dresden, Steinkopff, 1922.

[89] Carter, H. D., and Campbell, A. N., *Trans. Electrochem. Soc.*, **63**, 419 (1933).

[90] Plotnikow, I., *Z. Elektrochem.*, **35**, 434 (1929). For a discussion of syntheses conducted in electric discharges, see Schenk, P. W., *Angew. Chem.*, **50**, 535 (1937).

[91] See also Nitchie, C. C., *Ind. Eng. Chem. (Anal. Ed.)*, **1**, 1 (1929); Wilhelm, H. A., *Ibid.*, **10**, 211 (1938).

[92] Heyne, G., *Angew. Chem.*, **45**, 612 (1932); Moritz, H., *Zentr. Mineral. Geol.*, **1935A**, 284; Roach, F., *Nature*, **139**, 547 (1937); Russanow, A., *Z. anorg. allgem. Chem.*, **219**, 332 (1934); Webb, D. A., *Nature*, **139**, 248 (1937); Staud, A. H., and Ruehle, A. E., *Ind. Eng. Chem. (Anal. Ed.)*, **10**, 59 (1938); Owens, J. S., Peake, J. S., and Fowler, R. G., U. S. P. 2,117,497, May 17, 1938; *Chem. Abs.*, **32**, 4889 (1932). Dow Chemical Co., British P. 496,615, Jan. 3, 1938.

[93] Maltby, J. G., *Chem. & Ind.*, **1937**, 220; Standen, G. W., and Kovach, L., Jr., *Proc. Am. Soc. Testing Materials*, **35**, Pt. 2, 79 (1935); Gatterer, A., *Z. ver. deut. Ing.*, **80**, 129 (1936).

Chapter 6

Enclosed Vapor Arcs. The Quartz Mercury-vapor Arc

Enclosed gas and vapor arcs, of which the mercury-vapor arc is the most widely used, differ from the open arcs of the previous chapter in that the enveloping tube or bulb makes the pressure of the gas or vapor in the arc-conducting stream independent of that of the external atmosphere. The transparency of the envelope also limits the radiations available from such arcs. If, as is generally true, the arc vessel contains in liquid or solid form a relatively large quantity of the element, usually mercury, the vapor of which forms the conducting medium for the arc, the vapor pressure will depend upon the operating temperature of the arc. The voltage drop across the arc is dependent, as discussed in the preceding chapter, not only upon the nature of the electrodes, the cathode exerting the predominant effect, but also upon the nature of the gas or vapor, and its pressure. If the vessel contains a supply of unvaporized mercury, the pressure is the vapor pressure of the mercury at the temperature at any time, being very low when the arc is cool, and atmospheric or greater under certain conditions of operation. When the pressure is low, the arc fills the entire tube. When, after a starting period, the pressure of the mercury vapor rises, the arc becomes constricted to a narrow bright luminous stream, surrounded by dark mercury vapor. This absorbs certain of the mercury lines by self-reversal and thus alters the energy distribution between the various mercury lines.

The mercury arc emits predominantly only a few intense lines, superposed upon a weak continuous spectrum, which is neglected in much photochemical work. Under certain conditions, a less-important banded spectrum may be observed. About 6 per cent of the total energy is of wave-lengths less than 2900A. Figure 25 shows a photograph of the spectrum of a quartz tube mercury arc, and Figure 26 shows the relative intensities of the prominent lines of the spectrum. The relative intensities of these lines are modified by the operating conditions.

The condition of the conducting gas does not limit the current as does the resistance of an electric lamp filament, so that a resistance must always be placed in series with a gaseous conduction discharge in order to operate it.

Since the mercury arc came to be recognized as a reliable source of light of short wave-lengths, the number of types of lamps embodying its use has increased rapidly.

The early forms of the mercury arc were direct outgrowths from the open arcs discussed in the previous chapter and had both electrodes of mercury. In time, it was found advantageous to replace the anode by some other metal. More recently, the tendency has been to avoid the use of mercury cathodes as well, and employ only mercury vapor for the conduction of the discharge. Lamps of this type will be discussed in Chapter 8.

Early History of the Mercury Arc

Perkin[1] considers the observation that a brilliant light is emitted when mercury is vaporized in an electric arc to have been made originally by Wheatstone who, in 1835, described the characteristics of such a light before the British Association. Its illuminating power was not realized, however, until some time later, when in 1852 Jackson secured a patent for a mercury lamp. The latter consisted of carbon electrodes, the lower one of which had a recess to hold a small quantity of mercury, the idea being to provide a non-consuming electrode. Binks about a year later produced and patented a lamp having two mercury electrodes which were enclosed in a glass case. Provision was also made for condensing the vaporized metal to the liquid condition again. Way patented a lamp (in 1856) which was described in the London *Times* of August 3, 1860, with the claim that it produced a more brilliant light than had ever been seen before.

Harrison, in 1857, developed a lamp in which a carbon rod was suspended over a cup of mercury. In another form of lamp, mercury was caused to drop on a carbon rod. Difficulties were encountered in obtaining a steady arc, although Harrison endeavored to overcome these by means of an electro-mechanical device. In 1867, Siemens made a mercury lamp which had a vibrating electrode dipping into a mercury cup. The light of this lamp was, however, of an intermittent nature. Siemens' idea was to employ this lamp for lighting buoys at sea, but apparently the device was never used for this purpose. The next attempt to produce a mercury lamp appears to have been made in 1875 by Prosser. It was a combined carbon and mercury lamp, the object being to overcome flickering, which was an unpleasant feature of the original arc lamps. Among the various other attempts to produce a satisfactory lamp must be mentioned that of Rapieff in 1879. This lamp contained a condensing chamber for the mercury vapor, and could be started by shaking the mercury or by an electro-mechanical arrangement.

In 1892, Arons showed that an arc could be produced by passing a direct current through mercury in an evacuated tube. The Arons lamp, which was five feet long, was started by tilting and, therefore, must have required a very large quantity of mercury. According to Axmann,[2] the later types of mercury vapor lamps are based on Arons's investigations upon low-pressure arcs. Thus, in 1892, Dowsing and Keating made a lamp in which an alternating current was passed through a Geissler tube containing mercury. They found it advisable to warm the mercury in order to vaporize it before starting the lamp.

The object of most of the early workers was the production of a lamp for visible illumination. The first lamp to attract attention in this connection was one displayed by Peter Cooper-Hewitt before the American Institute of Electrical Engineers at a meeting in April, 1901.[3] This lamp, the result of long experimenting, is said to have been installed first in the composing rooms of the New York *Evening Post* in 1903. Many practical difficulties, such as the inherent instability of the arc, changes in mercury vapor pressure with operating temperature, and distillation of the mercury from certain portions of the lamp, were encountered. Cooper-Hewitt later devised a lamp in which the mercury was cooled and condensed at about the same speed as that at which it vaporized.

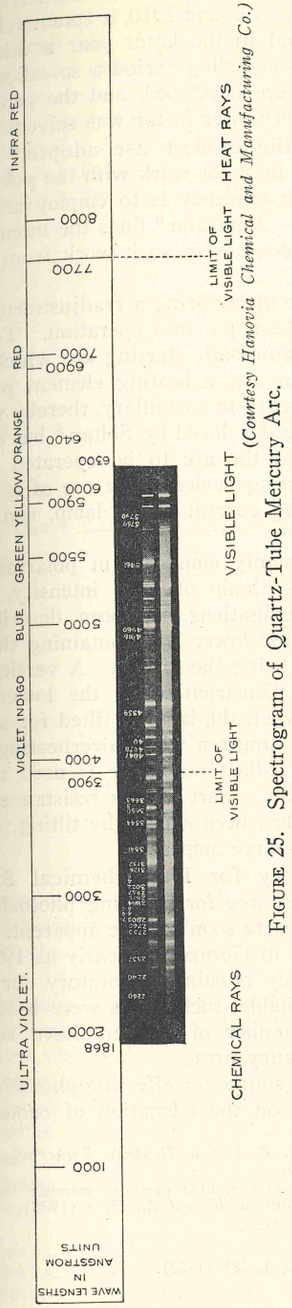
The development of the lamp as an illuminating source for factories and drafting rooms lies beyond the scope of this book, except insofar as modifications have been successfully applied to the mercury arc in a quartz tube employed for ultraviolet emission. The reader interested in the development of the Cooper-Hewitt lamp, which is a long arc operating at a low mercury-vapor pressure, should consult the articles by Buttolph[4] of the Engineering Department of the General Electric Vapor Lamp Co. He points out that during the years 1902-07, the condensing chamber

[1] Perkin, F. M., *Trans. Faraday Soc.*, **6**, 199 (1911).

[2] Axmann, *Z. Phys. diatetische Ther.*, **13**, 470 (1909-10).

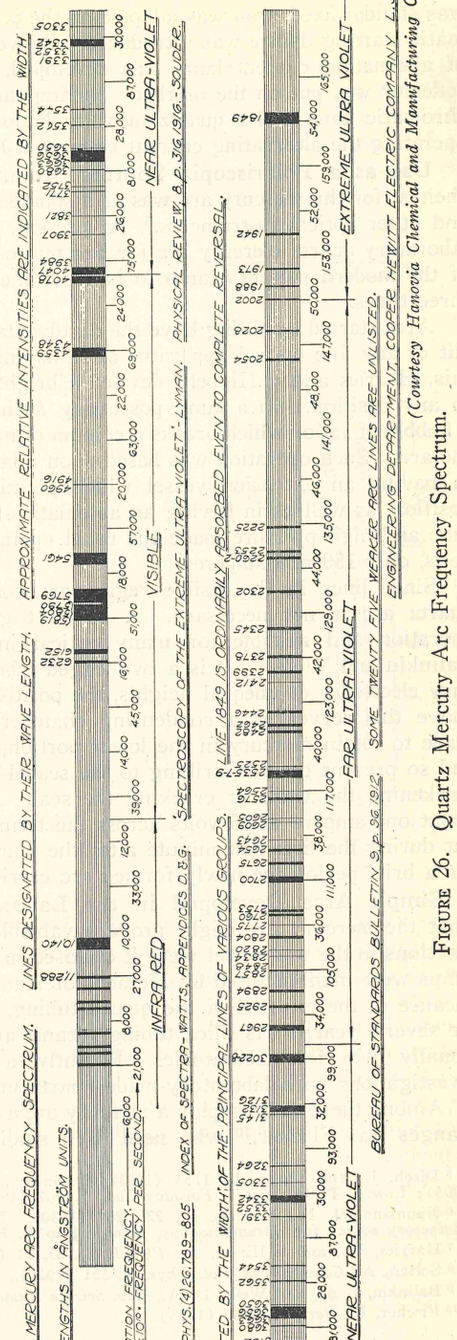
[3] Buttolph, L. J., *Trans. Electrochem. Soc.*, **65**, 143 (1934).

[4] Buttolph, L. J., *Gen. Elec. Rev.*, **23**, 741, 858 (1920); *Rev. Sci. Instruments*, **1**, 487 (1930); *Trans. Electrochem. Soc.*, **65** (1934), 143; *Trans. Illum. Eng. Soc.*, Preprint, 1932; **30**, 147 (1935). (See also, Ferguson, J. B., "The Quartz Mercury Vapor Lamp": London: Lewis and Co., Ltd.; and also Pierce, R. F., *Illuminating Engineer*, **6**, 133 (1911).



(*Courtesy Hanovia Chemical and Manufacturing Co.*)

FIGURE 25. Spectrogram of Quartz-Tube Mercury Arc.


QUARTZ MERCURY ARC FREQUENCY SPECTRUM.
LINES DESIGNATED BY THEIR WAVE LENGTH.
APPROXIMATE RELATIVE INTENSITIES ARE INDICATED BY THE WIDTH
WAVE LENGTHS IN ÅNGSTRÖM UNITS.
OSCILLATION FREQUENCY
SCALE x 10⁶: FREQUENCY PER SECOND
INFRA RED
VISIBLE
NEAR ULTRA-VIOLET
PHYSICAL REVIEW, S.P. 3:6, 1916 - SOUDER.
ANN. d. PHYS. (4) 26, 789-805
INDEX OF SPECTRA - WATTS, APPENDICES O.S.G.
SPECTROSCOPY OF THE EXTREME ULTRA-VIOLET - LYMAN.
INDICATED BY THE WIDTH OF THE PRINCIPAL LINES OF VARIOUS GROUPS.
* LINE 1849 IS ORDINARILY ASSOCIATED EVEN TO COMPLETE REVERSAL.
FAR ULTRA-VIOLET
EXTREME ULTRA VIOLET
NEAR ULTRA-VIOLET
BUREAU OF STANDARDS BULLETIN 9, P. 36, 1912.
SOME TWENTY FIVE WEAKER ARC LINES ARE UNLISTED.
ENGINEERING DEPARTMENT, COOPER HEWITT ELECTRIC COMPANY, U.S.A.

(*Courtesy Hanovia Chemical and Manufacturing Co.*)

FIGURE 26. Quartz Mercury Arc Frequency Spectrum.

was standardized, iron was adopted as the positive electrode material, and an automatic starting device was introduced. Between 1907 and 1910, a commercial form of alternating current lamp was developed, and in the latter year a fluorescent reflector was put on the market. During the succeeding period a so-called orthochromatic lamp and a quartz mercury lamp were developed, and the problem of operating the alternating current lamp on a high power factor was solved.

Use as a Polariscopic Source. About the earliest use adopted by the chemist for the mercury arc was as a source of light for work with the polariscope and other optical instruments.[5] At present, the tendency is to employ any usual laboratory quartz mercury arc for this purpose. Naumann [6] finds the intense light of the modern mercury lamp to increase the accuracy of such work from two to three times.

Arcs started by tilting have the disadvantage of requiring a readjustment of the slit of any fine optical apparatus after having been put into operation. To avoid this, Harries and v. Hippel [7] devised a bright, automatic starting arc which burns in any position. In a lamp possessing such an arc, a heating element produces a bubble of vapor which breaks a column of mercury in a capillary, thereby starting the arc. Such operation was based upon a lamp developed by Soltan [8] but differed in having an extension vessel which permitted the arc to be operated in any position, as well as in having an automatic starting device. The use of a narrow tube and high pressure made the usual operating current of the lamp, run at 110 volts, only 150 milliamperes.

Since lines in the visible region are commonly employed in polarimetry, a quartz arc is not necessary. A compact glass lamp of high intensity, steady operation and suitable for many optical investigations has been described by Balinkin and Wells.[9] It is a two-legged tube, the lower legs containing the mercury electrodes of unequal heights, the positive being the higher. A vertical tube above this serves as a condensing chamber. Constrictions in the lower limbs serve to retain mercury in the lower portions when the lamp is tilted for starting and so prevent the arc striking to the sealed-in tungsten wires, overheating them, blackening the walls or cracking the seal. A ballast resistance is used to keep about one ampere at 35 volts across the terminals. Part of this resistance is cut out during the first half minute after the lamp has been started by tilting, so that for a brief period the newly formed arc carries three amperes.

Simple Arcs Developed in the Laboratory for Photochemical Studies. That the mercury arc might prove a valuable source for studying photochemical reactions in the ultraviolet were it enclosed in quartz soon became apparent. Such lamps were manufactured by Heraeus of Hanau in Germany as early as 1905 but, because of the expense of the quartz tubing, they remained laboratory curiosities for several years. As silica tubing became available, such lamps were used occasionally in a few laboratories. Recently, a number of workers have resumed investigations with laboratory-made quartz mercury arcs.

Among the first to employ a mercury arc as a source for effecting photochemical changes was Fischer,[10] who used it in studies on the formation of ozone. He

[5] Disch, J., *Ann. Phys.*, **12**, 1155 (1903); Schönrock, O., *Z. Verein. Deutsch. Zuckerind.*, **53**, 652 (1903); Lowry, T. M., *Trans. Faraday Soc.*, **7**, 267 (1912).

[6] Naumann, H. N., *Biochem. Z.*, **229**, 269 (1930). The Osram high pressure mercury lamp is a satisfactory source for ultramicroscopy, according to K. Hoffmann, *Kolloid Z.*, **83**, 9 (1938).

[7] Harries, W., and v. Hippel, A., *Physik. Z.*, **33**, 81 (1932).

[8] Soltan, A., *Compt. rend. Pol. Phys.*, **4**, 301 (1929).

[9] Balinkin, I. A., and Wells, D. A., *Rev. Sci. Instruments*, **3**, 388 (1932).

[10] Fischer, F., *Ber.*, **38**, 2630 (1905).

fixed an exhausted double-walled quartz cylinder B (Figure 27) with sealing wax into the neck of a surrounding cylindrical glass vessel A, connected with an air pump by the tube F. The anode consisted of an iron ring K, surrounding the quartz cylinder and suspended by means of two platinum wires fused into the walls of the glass vessel. Mercury in the bottom of the latter served as cathode. The lamp was operated at 20 volts and 5 amperes, and was started by means of an induction coil. Arrangements were made to cool the lamp both internally and externally, so that the temperature in the interior of the lamp was kept down, thus maintaining a low density of the mercury vapor.

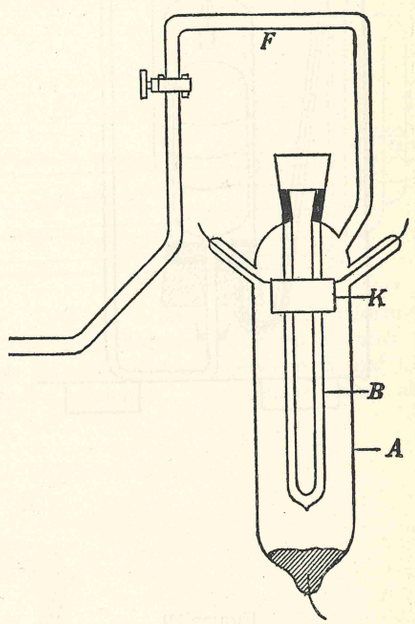


FIGURE 27.

Fisher's Lamp for Formation of Ozone.

Chapman, Chadwick and Ramsbottom [11] employed a similar principle in effecting gas reactions in a quartz bulb (Figure 28) enclosed in a glass mercury lamp in which the cathode was a pool of mercury and the anode a short cylinder of iron suspended in the upper part of the exhausted glass container. A somewhat more complex lamp, although very similar in principle, was used by Coehn and Becker [12] in their work on the oxidation of sulfur dioxide. (Figure 29.) The lamp consists of a glass vessel (4) in which the double-walled quartz vessel (2 and 3) is placed. A mercury seal is used at the top of the vessel (4). The lamp is located in the water-jacket or cooling vessel (5). To make the burning uniform a magnet (M) is placed in a glass tube in the lamp as shown. A quartz tube (1) is inserted in the vessel (2) through which gases may be passed by means of the inlet and outlet tubes (G).

Weigert [13] bent the arc tube into a U-shape, and arranged the apparatus for

[11] Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.*, **91**, 945 (1907).

[12] Coehn, A., and Becker, H., *Z. physik. Chem.*, **70**, 90 (1910); *Z. Elektrochem.*, **13**, 545 (1907).

[13] Weigert, F., *Z. physik. Chem.*, **80**, 67 (1912).

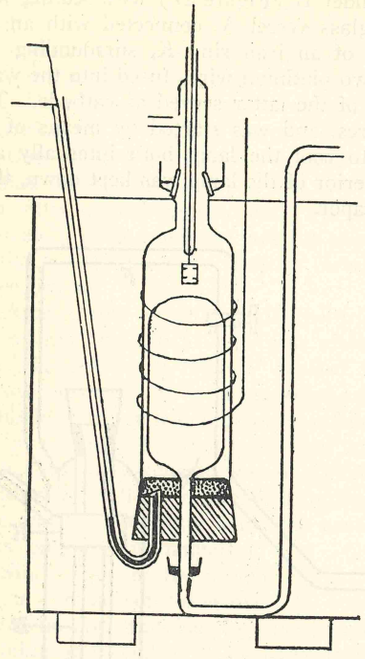


FIGURE 28.
Gas Irradiation Apparatus.

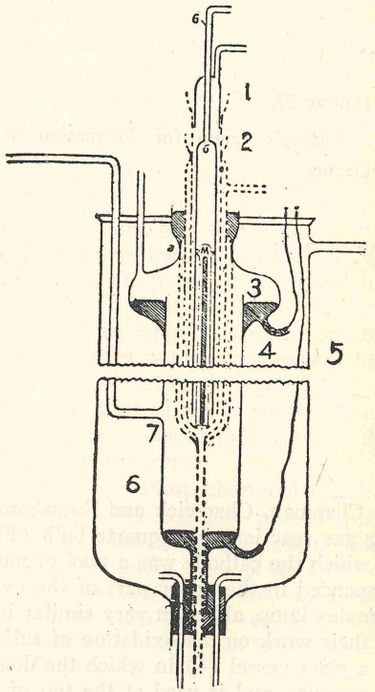


FIGURE 29.

water cooling so as to avoid the effects of heat (from the lamp) on the reactions under investigation. He surrounded the lamp by the reacting gases, the vessel containing them being in turn immersed in the cooling water. (Figure 30.) A mercury arc was formed in the inverted U-tube B between surfaces of mercury E_1 and E_2, electrical connection being made at K_1 and K_2. The apparatus was mounted in a watertight casing having a quartz plate serving as a window if external exposures were to be made also.

Bovie [14] constructed several lamps for biological experiments; these were not difficult to make and the design could be altered readily to suit particular requirements. Figure 31 shows a simple form based upon a lamp made by Kraus. A is

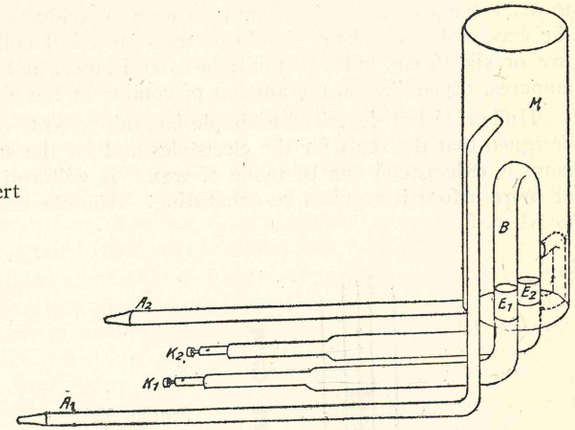


FIGURE 30.
Lamp Employed by Weigert for Treatment of Gases.

a quartz tube one centimeter in diameter. One end is bent downward to form the positive electrode C. A quartz tube of the same diameter is sealed in, near the other end, to form the negative electrode B. The distance between B and C is about 10 cm. The end of the tube A forms a condenser. The lamp is sealed, after

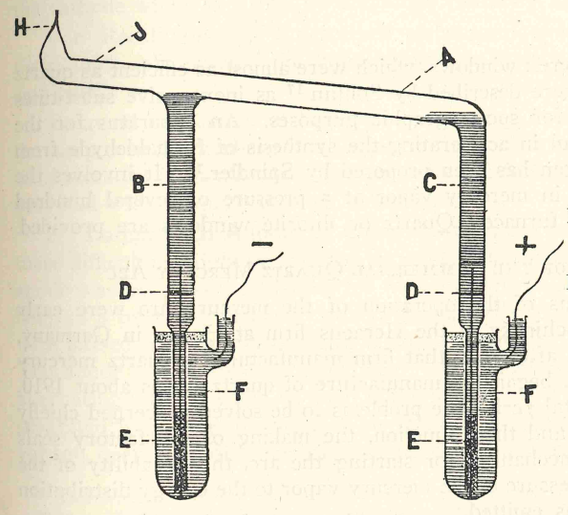


FIGURE 31.
Lamp Used by Bovie for Biological Work.

exhaustion of gases at H. The tube A should be inclined to the horizontal position at an angle of 6° to 7°, the end (J) being higher, so that the condensed mercury

[14] Bovie, W. T., *J. Biol. Chem.*, **20**, 315 (1915).

will flow back into C. Pieces of five-millimeter quartz tubing are sealed to the lower ends of B and C. These in turn are set in mercury cisterns F,F (made of glass); test tubes may be used. The small tubes are sealed at E. The detail of the seal is shown in Figure 32. A bulb of wax on the outside is necessary in order to make the seal air-tight. The iron wire D conducts the electric current through the wax seal. The lamp should be used on a 110 volt direct-current circuit with five or six 16 c.p. bulbs in multiple as resistance, and will carry from 1.25 to 1.5 amperes, depending on the amount of cooling at the electrodes B and C.

Hulbert [15] has described a simple laboratory lamp made of Pyrex or quartz, so designed that the seals for the electrodes and for the stopcock (through which the lamp is exhausted) can be made of wax. It will run normally for twenty hours or more before it requires re-exhausting. Another easily constructed lamp is due to Allen.[16]

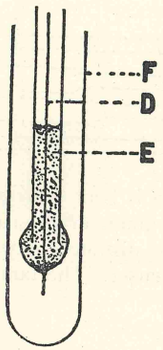


FIGURE 32.

Construction of Seal.

Arcs in glass with thin Pyrex windows, which were almost as efficient as quartz in transmitting ultraviolet, were described by Sonkin [17] as inexpensive substitutes for the quartz mercury arc for spectrographic purposes. An apparatus for the production of radiations useful in accelerating the synthesis of formaldehyde from carbon monoxide and hydrogen has been proposed by Spindler.[18] It involves the production of very hot arcs in mercury vapor at a pressure of several hundred kilograms, in a special steel furnace. Quartz or fluorite windows are provided.

THE DEVELOPMENT OF THE COMMERCIAL QUARTZ MERCURY ARC

Fundamental investigations of the operation of the mercury arc were early conducted by Küch and Retschinsky of the Heraeus firm at Hanau in Germany, about 1905 to 1907. Shortly after this, that firm manufactured a quartz mercury arc. The Cooper-Hewitt Co. began the manufacture of quartz lamps about 1910. During the early developmental period the problems to be solved concerned chiefly the nature of the electrodes and their function, the making of satisfactory seals for the electrical leads, the mechanism for starting the arc, the instability of the arc, and the relation of the pressure of the mercury vapor to the energy distribution and intensity of the radiations emitted.

[15] Hulburt, E. O., *J. Opt. Soc. Am.*, **12**, 519 (1926).
[16] Allen, A. J., *Science*, **83**, 336 (1936).
[17] Sonkin, S., *J. Opt. Soc. Am.*, **19**, 65 (1929).
[18] Spindler, H., U. S. P. 1,880,333, October 4, 1932.

NATURE OF THE ELECTRODES

1. Lamps With Both Electrodes of Mercury. As the early arcs were a direct outgrowth of the carbon or iron arcs, it was usually felt necessary to have both of the electrodes pools of mercury. The arc was formed by so tilting the lamp as to make a mercury contact between the two pools and then in some manner breaking the column of mercury, the newly formed arc driving the mercury back into the pools in the electrode vessels.

Such lamps required elaborate temperature control by means of metal heat-radiating fans to maintain the proper distribution of mercury between the electrodes, or else it was necessary to introduce a suitable condensing chamber for the mercury. Bachmann [19] claimed the elimination of this difficulty by using an anode of metal or alloy, the surface of which is amalgamated anew from time to time by means of mercury supplied from near the electrode.

Kent and Lacell [20] equalized the anode and cathode temperatures by bending the quartz tubes so that the electrodes were adjacent to each other. This was believed to prevent distillation of mercury from the hotter anode to the cathode, thereby extinguishing the arc. Belleaud and Barrollier [21] used a heat conductor surrounding the electrodes to equalize their temperatures. They [22] described a lamp to be immersed in a liquid to be sterilized, in which the cathode was screened from the liquid so that it was permitted to reach a temperature equilibrium with the anode. The mercury at the cathode automatically adjusted itself to a height favorable for operation depending upon the characteristics of the tube and the supply current.

There seem to be no direct early determinations to show whether the anode is, indeed, hotter than the cathode. In the lamp of Kelvin, Bottomley and Baird, it is the cathode which is cooled by aluminum radiating fans.

Von Recklinghausen [23] described elaborate methods for ensuring the proper distribution of mercury in lamps having a series of electrodes, now seldom employed.

To avoid the danger of breakage by mercury "slaps" during transportation of the lamp, von Türkenburg [24] filled the entire burner with mercury. During operation, mercury is displaced by the arc into a deformable anode receiver of rubber, provided with adequate cooling arrangements.

2. Lamps with Anodes of Other Materials. It soon became apparent that these difficulties might be avoided by using other materials for the anode. An iron anode was proposed by Fischer for the lamp previously described. Tian [25] made a lamp of a tube of transparent quartz through the center of which an insulated iron wire passed making contact with a drop of mercury (the cathode) at the bottom. The anode was a small iron cylinder. Ordinarily, direct current was used, but alternating current could be used if the anode was made double, *i.e.*, of two plates separated by a sheet of mica. This form of lamp had the advantage, besides low voltage operation, of being of a shape convenient for immersion in liquids. An

[19] Bachmann, P., German P. 336,570, May 11, 1920; *J. Soc. Chem. Ind.*, **40**, 575A (1921).
[20] Kent, H. A., and Lacell, H. G., British P. 21,834 (1908).
[21] Belleaud, R. L. M., and Barrollier, J., British P. 168,022, Dec. 10, 1920; 211,455, Jan. 25, 1924.
[22] Belleaud, R. L. M., and Barrollier, J., U. S. P. 1,656,898, Jan. 24, 1928.
[23] von Recklinghausen, M., U. S. P. 1,091,244, March 24, 1914, and 1,110,574, Sept. 15, 1914.
[24] von Türkenburg, F. R., U. S. P. 1,896,651, Feb. 7, 1933.
[25] Tian, A., *Compt. rend.*, **156**, 1063 (1913).

early Cooper-Hewitt lamp [26] also employed iron as the positive electrode. Asada [27] used a brine-cooled steel anode which extended into the interior of the lamp and kept the temperature from getting too high, even when the lamp carried 20 amperes.

Carbon was employed for this purpose by Axmann [28] and by Kerschbaum,[29] the latter using nickel-steel pins to bring in the current. Perkin [30] mentioned the use of a tantalum button, in conjunction with mercury, for starting.

Because of its high melting point, tungsten was employed as anode by Urbain, Scal and Feige.[31] It was then necessary to avoid even the smallest trace of oxygen or the walls of the enclosing vessel became darkened because of the production of volatile oxides. The use of tungsten was adopted in the lamps of George [32] and of Nutting.[33]

Sealed-in Leads. In order to produce vacuum-tight joints between the leading-in wires and quartz, Heraeus [34] proposed to use wires of iron or other metal having a temperature coefficient of expansion considerably greater than that of quartz. The diameter of the wire was to be such that the joint remained vacuum-tight at the highest anticipated temperature, the joint being reinforced by cements which melt at such a temperature. It was stated that an iron wire of 0.5 mm. diameter affords a vacuum-tight joint in quartz-glass at a dull red heat, and wires of 0.9 mm. diameter may be heated to 360°C. without the joint leaking.

Data on the expansion of fused quartz for temperatures up to 1000°C. were given by Holborn and Henning [35] who found that the mean increase of unit length for a rise of 1° is 0.00000054. Anderson [36] pointed out that Invar (an alloy with nearly the same coefficient of expansion as quartz) leads are unsatisfactory, since Invar melts below the fusing and working temperatures of quartz. Of other available metals, tungsten and molybdenum (coefficient of expansion 4.2×10^{-6}) are nearest to the thermal expansion of quartz, but molybdenum seals are only practicable in the case of very fine wires capable of carrying no more than one ampere. It was found that the tungsten seals which had been recommended by George could not be used. Lead or mercury seals had been described by the Thermal Syndicate. Anderson developed a method of working the quartz shell onto a core of a metal (tungsten, molybdenum, tantalum, platinum) of thermal expansion less than 9.0×10^{-6} and melting point higher than that of fused quartz (1750°C.), in which heat was applied to one end while the other was evacuated. The joint was tight at only one end; the slight space at the other was filled with a mixture of hydrocarbons. These must adhere [37] to both surfaces and not absorb water or gas, must have a low vapor pressure and change slowly in viscosity with temperature. A mixture of coal-tar pitch and residues of petroleum distillates, having a viscosity at 100°C. of 2000 dyne-seconds per square centimeter, was suggested.[38]

[26] *Elektrotechnische Z.*, **26,** 941 (1905).
[27] Asada, T., *Proc. Phys.-Math. Soc. Japan (3)* **12,** 167 (1930); *Chem. Abs.*, **25,** 254 (1931).
[28] Axmann, *Elektrotechnische Z.*, **26,** 627, 1182 (1905).
[29] Kerschbaum, F., U. S. P. 1,118,868, Nov. 24, 1914.
[30] Perkin, F. M., *Trans. Faraday Soc.*, **6,** 199 (1911).
[31] Urbain, E., Scal, C., and Feige, A., *Compt. rend.*, **152,** 255 (1911).
[32] George, H., U. S. P. 1,398,545, Nov. 29, 1921; *J. S. C. I.*, **41,** 49A (1922).
[33] Nutting, P. G., U. S. P. 1,320,087, Oct. 28, 1919, to Westinghouse Electric and Manufacturing Co.; *J. S. C. I.*, **39,** 8A (1920).
[34] Heraeus, German P. 336,014, Sept. 24, 1918; *J. Soc. Chem. Ind.*, **40,** 574A (1921).
[35] Holborn, L., and Henning, F., *Ann. Physik*, **10,** 446 (1903).
[36] Anderson, W. T., U. S. P. 1,909,797, May 16, 1933 (to Hanovia Co.).
[37] Anderson, W. T., U. S. P. 1,986,784, Jan. 8, 1935.
[38] See also British P. 356,056, Sept. 3, 1931, to Hanovia Co. for detailed discussion of a sealing arrangement. The use of rhodium coatings for the material to be sealed into quartz has recently been proposed by Harris, N. L., and Ryde, J. W., U. S. P. 2,113,984, April 12, 1938; British P. 477,462, Dec. 30, 1937; *Chem. Abs.*, **32,** 4299 (1938).

Lamps of the tungsten anode type may also be made by sealing the tungsten into glass, *e.g.*, Nonex glass (coefficient of expansion, 3.9×10^{-6}), which is then united to the quartz tube by a graded seal, employing Pyrex (3.2×10^{-6}).[39] Keyes and Kraus [40] described new glasses available for making graded seals for this purpose. They contained various proportions of titanium and vanadium oxides, as well as boron oxide. Successive rings cut from tubes of these glasses were fused onto the silica tube. In the earlier lamps employing complicated seals, overheating of the seals had to be avoided by the use of metal radiating fins. A general discussion of such joints has been given by Buttolph.[41] An ingenious method of sealing the annular ring guards at the anode and cathode of the silica tube so that they will be snug at the operating temperature of 400°C., and still not crush the silica tube on cooling, has been described by him in a patent which must be consulted for details.[42]

Methods of Starting the Discharge. Most quartz mercury arcs with either both electrodes or cathode only of mercury are started by tilting the lamp to form electrical contact by liquid mercury between the electrodes. Then, on again tilting the lamp back to its former position, the contact is broken and the arc is formed. Such a method was adopted in a water-cooled lamp of the Heraeus type used by Foster in 1906.[43]

Parisi [44] describes a mercury arc enclosed in a two-by-five-inch quartz bulb, equipped with an Edison socket, for operation on an ordinary direct-current lighting circuit. The lead-in wires, equipped with special mercury seals, are connected through wire resistance coils separated by quartz slabs, to two half-inch pools of mercury in separate enlargements at the base of the lamp bulb. The lamp is started by tilting. The coils then become incandescent, heat the mercury vapor, or retard its condensation, and thereby add to the intensity of the ultraviolet emitted.

The design of certain proposed forms of the mercury arc lamp precluded the ordinary method of starting by tilting, and a number of ingenious, but relatively seldom employed, starting devices have been suggested. An electromagnet served to bring an iron anode into contact with the mercury cathode in one type of lamp developed by the General Electric Co. as well as in that devised by Hulburt.[45] In the lamp of Gallois,[46] mercury in the initial position fills the quartz illuminating tube. When the current is applied, a coil attracts an armature connected by a rod with the tube, and turns the latter on its axis about 40°, whereby, in consequence of the shape of the tube, the mercury is divided into two portions and an arc is formed across the intervening space.

At one time, Buttolph [47] proposed to seal the arc tube to the leads by the mercury itself, the ends of the arc tube being extended into mercury-filled boxes. By means of pistons, the mercury could then be forced into the tube to form a contact and start the arc.[48]

Ulbrich [49] uses a wall to partly separate the anode mercury from the tube space;

[39] See also Goltstein, E., British Patent Application (void), 290,632.
[40] Keyes, F. G., and Kraus, C. A., U. S. P. 1,014,757.
[41] Buttolph, L. J., *J. Opt. Soc. Am.*, **11,** 549 (1925).
[42] Buttolph, L. J., British P. 376,686, July 14, 1932.
[43] Foster, G. W. A., *J. Chem. Soc.*, **89,** 913 (1906).
[44] Parisi, M., U. S. P. 1,954,888, April 17, 1934; 1,960,503, May 29, 1934 (to Goldberg, I.).
[45] Hulburt, E. O., U. S. P. 1,907,386, May 2, 1933.
[46] Gallois, J., *Bull. soc. encour, ind. nat. 121.*
[47] Buttolph, L. J., U. S. P. 1,831,998, Nov. 17, 1931.
[48] For special means of facilitating the starting of alternating current arcs, see Asada, T., *J. Inst. Elect. Eng., (Japan)*, **51,** 51 (1931); Steinmann, A., British P. 356,355, Sept. 10, 1931; Matouch, R., U. S. P. 1,750,482; Sperti, G., U. S. P. 1,889,079, Nov. 29, 1932.
[49] Ulbrich, W., U. S. P. 1,694,836, Dec. 11, 1928.

from the wall, one or more fine tubes extend the length of the tube, but are located outside of the luminous band. On tilting the lamp, mercury passes through the fine openings, so that it reaches the cathode from the end of the tube in a fine stream or streams. The use of the latter in starting avoids a sudden onrush of mercury, which might extinguish the newly formed arc, on restoring the arc to its normal position.

The lamp of Kent and Lacell [50] was started by electrically heating a small coil of wire placed around the arc tube. When started, the current was automatically cut off from the heating wire. This lamp, which was not evacuated, was burned on a 500 to 1000 volt circuit, and was extremely powerful. Preheating coils, which vaporize some of the mercury in about a minute to form contact with the anode and start the arc, have been used in various lamps. Their use also shortens the build-up period during which a steady ultraviolet intensity becomes established. A number of patents describe such devices.[51]

Electrical Starting Devices. For large-scale installations, for arcs of peculiar design to meet special irradiation conditions, and particularly for the long, low-pressure Cooper-Hewitt illuminating apparatus, the arc is usually formed by special auxiliary electrical equipment. In each instance there are involved, according to Buttolph,[52] who has reviewed the subject in detail, both the formation and maintenance of a hot spot on the cathode surface and the coincident ionization of mercury vapor between the electrodes.

With some types of arcs, the initial resistance was overcome by the aid of an induction coil, but this is usually impractical for large industrial arcs. In certain cases, however, in which the cathode spot has been formed and maintained by a small local arc to an auxiliary anode, or in which independently heated Wehnelt cathodes (see Chapter 8) are used, ionization of the vapor through the arc tube may be brought about by small Ruhmkorff coils of the kind commonly used as leak testers in high vacuum work with glass apparatus.

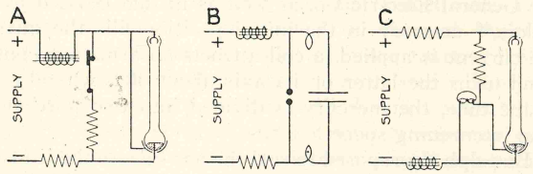


FIGURE 33. Circuits for Starting Mercury Arcs (Buttolph and Dana, *Review Scientific Instruments*).

Buttolph and Dana [53] state that the use of the operating reactance as a source of induced high voltage for arc starting (Figure 33, A) was described in patents applied for by Peter Cooper-Hewitt in 1900 to 1902. At this time the "inductance coil" was generally placed in the circuit adjacent to the arc anode, with an electrolytic interrupter or magnetically operated coil switch in multiple with the arc tube. Resistance in series with the interrupter switch kept the current sufficiently low so that it could

[50] Kent, H. A., and Lacell, H. G., British P. 21,834 (1908); Perkin, F. M., *Trans. Faraday Soc.*, **6**, 199 (1911).

[51] Thompson, A., U. S. P. 1,962,106, June 5, 1934; Hulett, M., U. S. P. 1,886,400, Nov. 8, 1932; Blake, G. J., and Leadbetter, G., British P. 294,288, July 23, 1928.

[52] Buttolph, L. J., *Rev. Sci. Instruments*, **1**, 498 (1930).

[53] Buttolph, L. J., and Dana, D. W., *Rev. Sci. Instruments*, **4**, 206 (1933).

be handled by the switch. The inductance of the lead wires, the capacity of the arc tube and the switch arc as indicated in the functional diagram B, constitute an elementary oscillatory circuit receiving its energy from the inductance coil. Such a circuit has a very high frequency and low efficiency. The effectiveness of the circuit depends upon the effectiveness of the interrupter switch, called a shifter. A high capacity mercury interrupter,[54] originally devised by Hewitt to take the place of the generally used spark-gaps in high-frequency generators, was adapted by Thomas [55] for use as a shifter switch in a starting circuit schematically shown in diagram C. When the apparatus is connected with the supply line, current flows through the auxiliary circuit, and the magnetic field of the inductance rotates the shifter switch forming a transient unstable arc in it. The resistance in series with the shifter is of an amount which makes the current too small to maintain the cathode hot spot. Furthermore, the stability of the shifter arc is decreased by the condenser between the mercury in the main arc and a tin-foil coating on the outside of the mercury chamber. When, after about 0.05 second, the arc is extinguished, the energy of the inductance is delivered as a single steep polarized wave-front impulse which tends to induce a negative potential of several thousand volts on the mercury cathode of the main arc. From an irregularity in the surface of the mercury formed by a coating of carborundum crystals fused into the glass, a localized discharge passes into the gas space and starts the main arc.[56]

Inert gases are also used in starting arcs. At first they were employed to strike the arc by breaking the mercury column when pumped into the lamp by some suitable arrangement.

In general, however, they serve as conductors through the discharge space until enough mercury has been vaporized to carry the arc. Bayle, Fabre and George [57] found that a direct-current, quartz mercury lamp containing argon at a pressure of 500 mm. of mercury, strikes instantaneously on application of the voltage and relights automatically if the arc should happen to be extinguished. Geffcken and Richter [58] believed argon the most suitable noble gas to use for this purpose. (See also Chapter 8.)

The Pressure of the Mercury Vapor. Various methods for improving the vacuum [59] or for exhausting the lamp space have been described.[60] During the earlier development of the Cooper-Hewitt and other commercial arcs, it was generally believed that to produce a stable arc, a low pressure of mercury vapor is essential. Kent and Lacell,[61] however, recognized that increased pressure is not the cause of the instability of the arc. Evidence in favor of the use of a higher mercury vapor pressure was afforded by Henri [62] in experiments which demonstrated that the ultraviolet radiation from a mercury vapor lamp becomes more intense as the tem-

[54] Pierce, G. W., *Proc. Am. Acad. Sci.*, **39**, 389 (1904).

[55] Thomas, P. H., U. S. P. 1,079,380 (1906).

[56] For details of means for securing mercury surfaces effective for starting, see patents of Winninghoff, W. J., U. S. P. 1,831,985-6 (1931) and 1,971,945, Aug. 28, 1934; British P. 288,737, April 19, 1928. Another description of an electrical starting mechanism is given by the Schering-Kahlbaum, A.-G., British P. 364,356 and 364,393.

[57] Bayle, E., Fabre, R., and George, H., *Bull. Soc. Chim.*, **37**, 89 (1925); *Rev. d'optique*, 1 (1925).

[58] Geffcken, H., and Richter, H., British Patent Application (void), 267,127. See for a limitation of the proportion of rare gas, N. V. Phillips' Gloeilampenfabrieken, British P. 474,192, Oct. 27, 1937; *Chem. Abs.*, **32**, 2854 (1938).

[59] von Recklinghausen, M., U. S. P. 1,110,576, Sept. 15, 1914; Thompson, W. P., British P. 28,757, Dec. 20, 1911; *Chem. Abs.*, **7**, 1846 (1913); Helbronner, A., and von Recklinghausen, M., British P. 14,129, June 10, 1910.

[60] Bovie, W. T., *J. Am. Chem. Soc.*, **37**, 1721 (1915); Waran, H. P., *J. Sci. Instruments*, **1**, 54 (1923).

[61] Kent, H., and Lacell, H., British P. 21,834 (1908).

[62] Henri, V., *Compt. rend.*, **153**, 426 (1911).

perature of the luminous tube is allowed to rise. By cooling the tube with water, the radiation was found to be fourteen times less powerful than with air-cooling, the same number of watts being consumed. A number of lamps were introduced in which the mercury vapor pressure was atmospheric or greater. These included the Cornu type lamps, the Kelvin, Bottomley and Baird lamp and others.[63] Bernhardt [64] built a mercury lamp which burned in carbon dioxide of up to 650 atmospheres pressure and carrying 400 amperes.

The U-shaped lamps of which mention has been made probably owed their greater relative output of ultraviolet rays to a higher vapor pressure of mercury due to a lessening of the cooling of the adjacent mercury electrodes rather than, as had been thought, to an altered distribution of mercury. The bent tubes of such lamps, however, tended to deteriorate or become opaque since the arc in making the bend

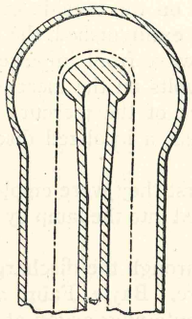


FIGURE 34.

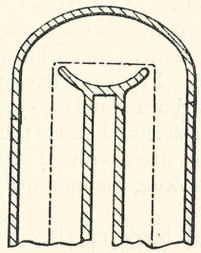


FIGURE 35.

does not follow the shape of the tube. Instead, as indicated by the dotted line of Figure 34, it tended to approach the side of the curved portion of the tube nearest the center of curvature, subjecting it to an extremely high temperature. To counteract such destructive action, this portion of the tube was made of increased thickness or projections (Figure 35) were added to divert the arc stream.[65] Von Recklinghausen [66] also described methods of prolonging the life of his lamps by lining the portion near the hot cathode spot with a highly refractory material such as "titanium zircon quartz."

COMMERCIAL MERCURY-VAPOR ARCS (MERCURY CATHODE TYPE)

Modern commercial mercury-vapor lamps with mercury cathodes are of two main types, those having a mercury anode and those having an anode of tungsten or other metal. The first is built along the lines of the Heraeus lamp. The Hanovia quartz mercury [67] arc lamp, Figure 36, consists essentially of three parts, the tube through which the arc plays, the anode vessel and the cathode vessel. The current is carried to the lamp through nickel rods ground into the side tubes of the electrode

[63] U. S. P. 1,343,037; British P. 129,022 and 129,702; *J. Soc. Chem. Ind.*, 622A (1919); Berlemont, G., *Bull. soc. encour. ind. nat.*, **133**, 254 (1921); *Chem. Abs.*, **15**, 2163 (1921); Stammreich, H., *Naturwiss.*, **12**, 744 (1926).

[64] Bernhardt, F., *Physik. Z.*, **27**, 713 (1926).

[65] von Recklinghausen, M., Helbronner, A., and Henri, V., U. S. P. 1,176,481, Aug. 29, 1916; 1,271,246, July 2, 1918.

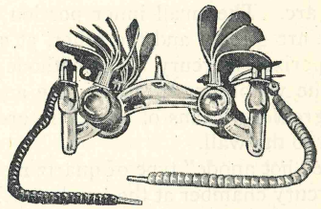
[66] von Recklinghausen, M., U. S. P. 1,188,587, June 27, 1916.

[67] Hanovia Chemical and Manufacturing Co. (A more recent type is discussed in Chapter 8.)

vessels. The ground-in joints are sealed with mercury. Small quartz tubes are used in the electrode vessels to avoid "hammering" of the mercury. The lighting of the lamp is effected by turning the lever slowly around from position to position so that a stream of mercury flows from anode to cathode, making a short circuit between the two poles. On breaking the stream, the arc is struck, and the level must be brought to its original position to allow the mercury to flow back into the

FIGURE 36.

Hanovia Lamp for Direct Current.



Courtesy Hanovia Chemical and Manufacturing Co.)

anode vessel. After lighting, the lamp may be turned again by the lever into a vertical position in which it can be continuously used. The arc may be used end-on in a horizontal position by viewing it from the anode end, or in a vertical position from above. On 220-volt lines the lamp may be burned at all potentials between the electrodes from 25-185 volts by means of a variable resistance of 55 to 95 ohms (depending on the type of lamp) connected in series; on 110-volt lines at all potentials from 25-80 volts by means of a variable resistance of 25 or 40 ohms. If the lamp is not required to burn at low voltages, resistances of 30 or 50 ohms and of 12 or 20 ohms suffice. At low potentials the arc or electric discharge fills the whole cross-section of the tube. With increasing potential, the cross-section of the arc diminishes more and more, and forms eventually a thread of some five millimeters diameter. The specific intensity of the visible and ultraviolet radiation is the same, and the economy equally as good in 110-volt as in 220-volt lamps. With constant external conditions the light exhibits a desirable degree of constancy. The Hanovia vapor lamp is also made for operation on alternating current, the difference in construction being that for this current it is necessary that there be two positive electrodes in place of the one ordinarily used for direct current.

Problems concerned with the design of pole vessels and the use of constrictions between these and the luminous tube to prevent alterations in the distribution of mercury during operation, have been studied by the Hanau firm.[68] By the use of a capillary at the anode, it is claimed that both vessels may be made of the same size and shape, and both may be completely filled with mercury. With alternating currents, two anode vessels have condensing chambers and separate connections by tubes with the luminous portion are necessary.

Anderson and Fraser [69] stated that in such lamps the proper temperature is usually maintained by radiation from metallic fins. If the lamp became too hot and the vapor pressure too high, the current would drop to values insufficient to maintain the cathode hot spot (which they believed to have a temperature of 2270°C.) and the arc would be extinguished. To avoid the necessity of using large volumes of mercury they proposed to immerse non-amalgamating metals of higher thermal conductivity such as wires, rods, meshes, tubes or plates of tungsten or molybdenum

[68] British P. 286,317, May 9, 1929.

[69] Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932, to Hanovia Co.

in the mercury in contact with the walls. Anderson [70] described methods of reducing the size of the container to one-half or one-third its previous size.

Water-cooled lamps are usually U-shaped, as in the case of those developed by Kent and Lacell. Bird [71] designed a burner in which the effects of expansion of liquid mercury upon the positions of the two mercury levels were minimized. By dividing the anode pool by inserting a smaller tube within the anode tube, it was possible to lessen the effect of the temperature of the pool upon the vapor pressure of the arc. The small inner portion at a high temperature served as the terminal for the arc stream and the other, at a reduced temperature, acted as a receiver for the vaporized mercury. The cathode pool was believed to exert a smaller influence upon the vapor pressure than the anode pool. The area of the cathode pool was made great by means of a bulb in order to lengthen the thermal path from the arc stream to the wall.

The "hot anode" type of quartz mercury vapor lamp, known as the "Uviarc," has no mercury chamber at the anode end.[72] In place of mercury, a tungsten target composed of a spiral formed of tungsten wire is used. The anode end is protected from mechanical injury by means of a metal cap which also serves to lead the current to the anode. The cathode end is reinforced with thick quartz to absorb the shock of the mercury vapor and is set at an angle which is claimed to reflect back into the luminous portion of the tube some ultraviolet rays which would otherwise escape. The cathode end is also protected by a metal cap through which the current is led to the mercury. The tungsten wire, serving to lead the current into the lamp, is sealed into the quartz tube by a graduated mixture of quartz and glass so that at the end there is practically pure glass, while the portion next to the quartz tube is practically pure quartz. It is claimed that this combination of glass and quartz provides a proper coefficient of expansion so that the loss of vacuum is prevented. Having only one mercury electrode, this lamp is capable of being operated in either a vertical or horizontal position, which in certain cases is of advantage. A slightly different design is employed when tungsten anode ("Uviarc") lamps are intended to be run generally in a vertical or nearly vertical position. The change is principally in the construction of the cathode chamber. The Uviarc is a direct current device. It may itself function as a rectifier.[73] An alternating current Uviarc with double anode is made for certain applications.

The development of Cooper-Hewitt lamps has followed two distinct courses for visible and for ultraviolet output. The original mercury arc has been developed as a long low-pressure arc for illumination of industrial establishments. LeBlanc [74] gave an early account of the construction, current consumption and efficiency of such lamps. Details of the more recent developments are to be found in the various articles of L. J. Buttolph cited in this chapter.

Our present concern is not, however, with the low-pressure illuminating arc, but rather with the high-pressure quartz arc just described. A small high intensity arc ("Labarc"), operating on 110 volts, either alternating or direct current, was described by Buttolph [75] in 1922. In it the effective light zone was one-quarter by one and three-quarter inches. It was especially suited for employment with filters, as a monochromatic light source. It was then shown that by introducing suitable

[70] Anderson, W. T., Jr., U. S. P. 1,902,936, March 28, 1933, to Hanovia Co.
[71] Bird, L. F., U. S. P. 1,952,306, March 27, 1934, to Hanovia Co.
[72] Cooper-Hewitt Electric Co., now General Electric Vapor Lamp Co.
[73] Buttolph, L. J., *Gen. Electric Rev.*, **13**, 741 (1920).
[74] LeBlanc, M., *Electrical Rev. and Western Electrician*, **57**, 1248 (1910).
[75] Buttolph, L. J., *J. Opt. Soc. Am.*, **6**, 1066 (1922).

resistance in series with the lamp it would function as a low-pressure arc giving only the strongest spectral lines. A detailed discussion of the operating conditions of the Uviarc is given in a following section.

A number of recent patents have been concerned with lamps, developed for specific purposes and with accessories as cabinets, etc. Burners enclosed in hoods may be prevented from overheating by sucking the hot air away by an electric fan attached to the upper part of the hood. According to Cooper,[76] this results in a saving of power. A cabinet for an arc for home use in therapy has been described by Link,[77] and a prepayment "coin-in-the-slot" time-switch control has been devised [78] for installations of the mercury arc in bath houses, therapeutic institutes and beauty parlors.

Therapy lamps adapted for introduction into various body cavities have been described by Philip.[79] They embody small U-tubes carrying the mercury arc, surrounded by a long, narrow quartz envelope with cooling water or gas. A number of other therapy arcs, not, however, adapted for introduction into orifices, designed by Nisbet [80] involved modifications of structural detail and new combinations of previously described principles.

To avoid the deposition of mercury on the luminescent part of a lamp intended to be submerged in water during use, Gourdon [81] located it in an evacuated vessel, the nipple of the luminescent part of the lamp passing through the wall of the vessel near the nipple of the vessel itself. This lamp was intended to be put to such curious uses as catching fish, maturing oysters and illuminating submarine operations.

An assembly of base, pedestal, hood with lips, and applicators suitable for ultraviolet therapy, has been patented by Chesney and MacLagan.[82] The Hanau firm [83] described a handle by which a therapy lamp could be carried about without danger of altering the distribution of the mercury.

The Theory of the Operation of the Mercury Arc

A. **Electrical Conduction Processes.** The general theory of the processes occurring in the arc has been treated in the previous chapter; this section deals with those processes which are especially characteristic of the arc in which the predominant conduction is by a mercury cathode and by mercury vapor in the space between the electrodes. Comparatively few investigations have been devoted to the nature of the manner in which the anode functions even in the case of the lamps of the Hanovia type in which the anode is mercury. As noted elsewhere, Compton [84] has stated that the entire problem is concentrated at the cathode, as other processes, especially those in the plasma, have been essentially explained by the work of Langmuir and Mott-Smith,[85] Tonks and Langmuir,[86] Eckart and Compton, [87] and Killian.[88]

1. *The Conduction of Current from the Cathode.* It was at first believed that the current was carried by electrons thermionically emitted from the cathode,[89] the temperature of which was then assumed to be about 2500°K. This had to be rejected when subsequent work showed that the cathode could not be hotter than

[76] Cooper, C. A., British P. 305,758, February 14, 1929.
[77] Link, D. C., U. S. P. 1,668,566, May 8, 1928.
[78] Bar, N., v. Recsey, N., and v. Recsey, E., British P. 382,349, October 27, 1932.
[79] Philip, G., British Patent Application (void), 298,903, October 15, 1928.
[80] Nisbet, J., British P. 248,796, March 11, 1926.
[81] Gourdon, G., British P. 390,108, March 30, 1933.
[82] Chesney, J., and MacLagan, H. P., U. S. P. 1,813,383, July 7, 1931, to McIntosh Electrical Corp.
[83] British P. 286,318, June 4, 1929.
[84] Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931).
[85] Langmuir, I., and Mott-Smith, H., *Gen. Electric Rev.*, **27**, 449,538, 616, 762, 810 (1924).
[86] Tonks, L., and Langmuir, I., *Phys. Rev.*, **34**, 876 (1929).
[87] Eckart, C. H., and Compton, K. T., *Phys. Rev.*, **24**, 97 (1924).
[88] Killian, T. J., *Phys. Rev.*, **35**, 1238 (1930).
[89] Stark, J., *Ann. Physik*, **12**, 673 (1903).

600°-800°.[90] Later calculations by Compton [91] indicate the surface temperature of the cathode spot not to exceed 200°C.

Earlier observers, as Güntherschulze,[92] gave large values for the rate of vaporization of mercury from the cathode, *e.g.*, 7.2×10^{-3} gram per ampere per second. The suggestion of Compton and van Voorhis that this was in part due to mechanical loss as spray was verified by von Issendorff, who found a corrected rate of less than $0.3\text{-}1.3 \times 10^{-3}$ gram per ampere per second. Kobel [93] placed it at only 0.017×10^{-3} and Nikiforov [94] places it at only 0.4 milligram per ampere per second. This indicates but a minute loss at the cathode. These new data show that the vapor pressures at the cathode spot must be considerably less than the atmosphere or more assumed in the earlier literature.

Slepian [95] suggested that the current might be carried by positive ions arising from thermal ionization of the vapor just outside the cathode; Compton, however, objected that this theory failed to suggest a mechanism for the input of energy into the assumed high temperature region. The currently accepted theory is that of Langmuir [96] of "field currents" due to a strong field concentrated at the cathode region. The minimum value of the field was calculated by Lamar and Compton [97] to be at least 7.6×10^4 volts per centimeter. Mackeown, assuming 5 per cent of the current to be carried by positive ions, calculates it to be 5×10^5 volts per centimeter. If 1.3×10^6 volts per centimeter be assumed necessary to give the observed cathode current density of 4000 amperes per square centimeter,[98] the cathode drop will occur within a distance of 10^{-5} centimeter. Lamar and Compton consider it to occur within a space of less than 1.76×10^{-4} centimeter, and give the cathode potential drop as about 10 volts (9.9 volts).[99] An earlier value of only 5.27 volts [100] was said to have been based upon the use of an erroneous probe method. Killian [101] also found about 10 volts and Gaudenzi [102] about 9 volts. Kommnick and Lübcke [103] find quite similar values, so that the mercury arc must be regarded as a special case of a low voltage arc. It was even found possible by Hebb [104] to maintain an arc in mercury vapor at only 1.7 to 1.8 volts although the 2537 line requires for its excitation (see below) 4.9 volts. Such an abnormal arc has been studied by Bär,[105] whose arc burned at 3.5 volts at 175°C. Unlike the earlier abnormal arcs, this was not due to oscillations, but to some positive space charge maintained before the cathode. Reverse fields sometimes play a part.[106]

After discussing in detail the attempts to determine from heat balance data the

[90] Mason, R. C., *Phys. Rev.*, **38**, 427 (1931); Compton, K. T., and van Voorhis, C. C., *Proc. Nat. Acad. Sci.*, **13**, 336 (1927); Compton, K. T., *Trans. Am. Inst. Elec. Eng.*, **46**, 868 (1927); Seeliger, R., *Physik. Z.*, **27**, 37 (1926); Lübcke, E., *Z. tech. Physik*, **10**, 598 (1929).

[91] Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931).

[92] Güntherschulze, A., *Z. Physik*, **11**, 74 (1922).

[93] Kobel, E., *Phys. Rev.*, **36**, 1636 (1930).

[94] Nikiforov, A. Y., *J. Exptl. Theoret. Phys. (U.S.S.R.)*, **6**, 168 (1936); *Chem. Abs.*, **31**, 14 (1937).

[95] Slepian, J., *Phys. Rev.*, **27**, 407 (1926).

[96] Langmuir, I., *Science*, **58**, 290 (1923); *Gen. Electric Rev.*, **26**, 735 (1923); see also Mackeown, S. S., *Phys. Rev.*, **34**, 611 (1929).

[97] Lamar, E. S., and Compton, K. T., *Phys. Rev.*, **37**, 1069 (1931); see also Gvosdover, S. D., *Physik. Z. Sowj.*, **7**, 274 (1935).

[98] Güntherschulze, A., *Z. Physik*, **11**, 74 (1922).

[99] Lamar, E. S., and Compton, K. T., *Phys. Rev.*, **37**, 1069 (1931).

[100] Stark, J., Retschinsky, T., and Shaposchnikoff, A., *Ann. Physik*, **18**, 213 (1905).

[101] Killian, T. J., *Phys. Rev.*, **31**, 1122 (1928).

[102] Gaudenzi, A., *Brown-Boveri Rev.*, **16**, 303 (1929).

[103] Kommnick, J., and Lübcke, E., *Physik. Z.*, **33**, 215 (1932).

[104] Hebb, T. C., *Phys. Rev.*, **16**, 375 (1920); see also Yao, Y. T., *Phys. Rev.*, **21**, 1 (1923).

[105] Bär, R., *Z. Physik*, **31**, 430 (1925).

[106] Rudy, R., *J. Frank. Inst.*, **201**, 248 (1926); v. Dziewulski, H., *Z. Physik*, **69**, 366 (1931).

fraction of the current carried by electrons and by positive ions at the cathode, Compton [107] concluded these to be futile since the range of certain quantities needed in the calculations was not known. It was, however, possible to show that the heat balance may be made consistent with Langmuir's theory and with the known facts of ionization by making certain reasonable assumptions regarding the unknown fraction of energy returned to the cathode by unelectrified carriers such as neutral atoms in various energy states, or by radiation.

The cathode spot moves rapidly on the mercury surface as it becomes conditioned and migrates to a neighboring spot where the mercury surface is contaminated by impurities and where the electrons can be more readily extracted. The mercury surface becomes depressed and the electrons probably come from the irregular edge of the crater, which is then immediately depressed, due to the vapor pressure of the mercury, heated by the bombardment of positive ions at the cathode spot. This would also account for the rapid movement of the cathode spot, since the electrons always come from the edge of the crater, which is then depressed by the increased vapor pressure at that point. Tonks [108] described methods of preventing this unsteadiness at the cathode end of the positive column by the use of wires of certain metals, especially molybdenum, the cathode spot being limited to the line of wetting. From the spectral distribution of the radiations from such anchors, it was suggested that there might be a region of "hot" ionized gas close to the cathode. Cravath [109] studied the behavior of the mercury vapor arc with a jet of liquid mercury as cathode, but was unable to obtain a stationary cathode spot on the jet.

It has been found that the mercury arc can be operated with the cathode frozen at −70°C, the voltage being not much higher than that for the normal operation of the arc.[110] Newman [111] has also studied the operation of the mercury arc at liquid air temperatures, his experiments supporting the idea that the fraction of the current carried by electrons depends on the vapor pressure. The parts of the arc immersed in liquid air were not luminous, but there was a brilliant cathode spot.

2. *Conduction Processes in the Plasma.* Little need be added here to the general discussion of this topic given in the previous chapter. As in general in the gaseous discharge, the tension, U, on the electrodes of a mercury arc is a linear function of the arc length l, *i.e.*, $U = A + Bl$, in which A is the sum of the anode and cathode drops of potential and B is the voltage gradient in the arc. Pawlikowski [112] found the mean velocity of all electrons to be constant throughout the whole width of the positive column, although in the immediate vicinity of the cathode two groups of electron velocities were noted.

The theory of the striated glow discharge in mercury vapor was studied by Compton, Turner and McCurdy.[113] In this work, attention was drawn to the importance of cumulative ionization in the striations. This concept has since been extended to the phenomena in the ordinary discharge.

There have been many divergent statements in regard to the transfer of mercury

[107] Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931); Compton, K. T., and Langmuir, I., *Rev. Modern Physics*, **2**, 184 (1930). For other earlier attempts, see Güntherschulze, A., *Z. Physik*, **31**, 509 (1925); Seeliger, R., *Physik. Z.*, **27**, 22 (1927); *Elektrotech. Z.*, **49**, 853 (1927); Compton, K. T., and van Voorhis, C., *Proc. Nat. Acad. Sci.*, **13**, 336 (1927); v. Issendorf, J., *Physik. Z.*, **29**, 857 (1928). See also Gehrts, A., and Vatter, H., *Z. Physik*, **79**, 421 (1932), and Weizel, W., Rompe, R., and Schon, M., *Z. Physik*, **112**, 339 (1939).

[108] Tonks, L., *Physics*, **6**, 294 (1935).

[109] Cravath, A. M., *Phys. Rev.*, **36**, 1480 (1930).

[110] Kawa, J., *Acta. Phys. Polonica*, **1**, 427 (1932); *Chem. Abs.*, **28**, 4667 (1934).

[111] Newman, F. H., *Phil. Mag.*, **18**, 607 (1934).

[112] Pawlikowski, J., *Acta. Phys. Polonica*, **2**, 59 (1933); *Chem. Abs.*, **28**, 7155 (1934).

[113] Compton, K. T., Turner, L. A., and McCurdy, W. H., *Phys. Rev.*, **24**, 597 (1924).

between the electrodes of the direct-current arc. Perot,[114] who made one observation of the change in mercury levels in an inverted U-arc, believed all of the current to have been carried by univalent mercury ions. Matthies,[115] however, found no mercury transfer other than that due to thermal processes and believed the conduction to be entirely electronic. Other workers took intermediate positions. Güntherschulze[116] believed half of the current carried by electrons and half by ions and Schottky and von Issendorff,[117] that 80 per cent was carried by ions. The more recent calculations of Langmuir have shown that the positive ion current is not more than 1/340 to 1/605 of the electron current density. Tonks[118] states that of the current carried by mercury ions 50 per cent is by doubly and 12 per cent by triply charged ones.

Forbes and Leighton,[119] using a lamp which was too hot to allow condensation of mercury to occur on the walls, found the ratio between the gram atoms of mercury transferred from the anode to the cathode and the faradays passing through the lamp to be sensitive to cathodic cooling and that mercury can migrate against considerable temperature gradients. Extrapolation of their results to the lowest voltage gradients and pressures indicated a minimal mercury transfer and an insignificant role for the positive ions. But, as the voltage gradient and the pressure rise, the positive ion current appears to gain on the electron current. At five volts per centimeter, the ratio has reached five, almost irrespective of the current, and remains near that value up to 25 volts per centimeter and a pressure of three atmospheres. Elenbaas[120] has discussed the theory of the gradient of the high-pressure mercury discharge.

3. *The Pressure in the Arc.* Küch and Retschinsky[121] measured over twenty internal pressures in an arc 12 mm. in diameter. Between 3 and 18 volts per centimeter, the pressure rose from 38 to 1500 mm., the current varying between 4.1 and 5.05 amperes; they gave, however, no quantitative correlation between the pressure and other variables.

Forbes and Leighton,[122] realizing that the electrical conditions depend on the resistance, pressure and the efficiency of air and water-cooling, presented graphs relating the pressure to the voltage gradient for arcs of 9 and 2 mm. diameter, (see Section on Constricted Arcs, Chapter 6) each carrying various currents. They concluded

(a) The pressure is a function of the cross section, voltage gradient and current, but not of the arc length or the relative cathode and anode temperatures.

(b) In spite of wide differences in the arc cross section and the current carried, the pressure changed about 140 mm. for a unit change in the voltage gradient, and the curves became nearly parallel at pressures greater than two atmospheres.

(c) For a given lamp at constant voltage, the pressure is very roughly proportional to the logarithm of the current.

(d) At low voltage gradients, the ratio of pressure to cross section for a given current strength is nearly the same for the constricted arc as for the normal arc, but at higher voltage gradients, the ratio is greater for the constricted arc.

[114] Perot, A., *J. Phys.* (5), **1**, 609 (1911).
[115] Matthies, W., *Ann. Physik,* **37**, 721 (1912).
[116] Güntherschulze, A., *Z. Physik,* **11**, 75 (1922); **31**, 509 (1925).
[117] Schottky, W., and von Issendorff, J., *Z. Physik,* **26**, 85 (1924).
[118] Tonks, L., *Elec. Eng.,* **53**, 239 (1934).
[119] Forbes, G. S., and Leighton, P. A., *J. Opt. Soc. Am.,* **12**, 53 (1926). For the clean-up of mercury by the walls, Kenty, C., *J. Applied Phys.,* **9**, 765 (1938).
[120] Elenbaas, W., *Physica,* **1**, 673 (1934); **2**, 757, 767, 787, 807 (1935); **4**, 279 (1937); *Phys. Rev.,* **55**, 294 (1939).
[121] Küch, R., and Retschinsky, T., *Ann. Physik,* **20**, 563 (1906).
[122] Forbes, G. S., and Leighton, P. A., *J. Opt. Soc. Am.,* **12**, 53 (1926).

(e) Had there been an "anode pressure" as suggested by Hamburger,[123] and by Skaupy,[124] it would have been noted.

4. *Electrical Operating Characteristics of the Mercury Arc.* The early knowledge of this field was summed up by Buttolph.[125] The following account is based largely upon his more recent accounts.[126]

On starting the Uviarc lamp, the vapor pressure is low, as the lamp is cool, and the current is high and the voltage low. The lamp requires a short time to reach normal operating conditions, depending upon the heat capacity of the mercury cathode and arc tube, and upon the initial arc energy. As the temperature rises, the vapor pressure and the voltage follow, while the current drops. Normal operation is reached when heat is radiated from the burner at such a rate that the vapor pressure no longer rises. In the upper left hand corner of Figure 37 the change in voltage and in current which occur during the first few minutes after starting are separately plotted and show clearly the way in which the arc comes to normal operation. As the starting current and the final arc voltage are each determined by the series resistance, a family of starting curves for different values of the series resistance is given in the main portion of the figure. The locus of the terminations of these curves at operating equilibrium at 25°C., H-L, is called the stationary or static characteristic curve for that arc at that temperature.

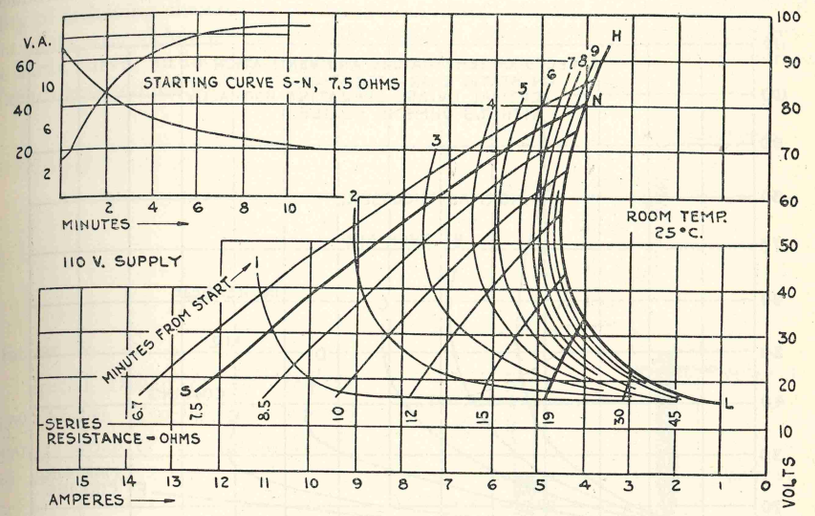


FIGURE 37. Starting and Operating Curves of Vertical Uviarc (Buttolph, *Review of Scientific Instruments*).

During the transition from the low pressure arc starting condition to the high pressure arc, there occurs a striking change in the appearance of the luminous arc column. As seen through a dark filter, the principal light source becomes concentrated in the center of the arc tube as a slender cord of great brilliancy. In this

[123] Hamburger, L., *Proc. Acad. Sci. Amsterdam,* **25**, 1045 (1917).
[124] Skaupy, F., *Verh. Deut. Phys. Ges.,* **19**, 264 (1917).
[125] Buttolph, L. J., *Gen. Electric Rev.,* **23**, 741, 858, 909 (1920).
[126] Buttolph, L. J., *Rev. Sci. Instruments,* **1**, 487 (1930); *Trans. Illum. Eng. Soc.,* **28**, 153 (1932).

condition there is about 25 volts drop per inch in the arc as compared with approximately 1½ volts per inch in the low-pressure arc.

The Uviarc may be operated at various arc voltages from about 20 volts up to a maximum, characteristic of each size of lamp. The static characteristic curve H-L expresses the relationship between the arc voltages and the corresponding normal current. A significant feature is the steepness of the curve. The temperature at which there is normal operating equilibrium is determined largely by the temperature of the room and the ventilation of the burner. For example, with a given maximum burner voltage determined by the line voltage and the series resistance, the current normal for the design is increased by cooling the burner, as indicated by Figure 38. It is thus evident that the temperature of operation introduces

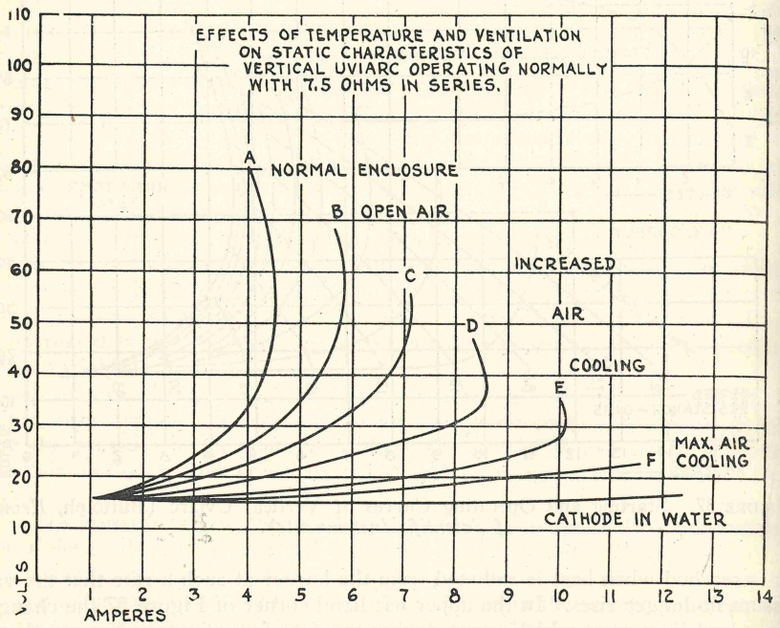


FIGURE 38. Effect of Temperature and Ventilation (Buttolph, *Review of Scientific Instruments*).

another variable. For this reason, the 220-volt horizontal Uviarc requires about 4.5 amperes at 165 volts between the electrodes when operated in open air, while its normal current when enclosed is only about 3.75 amperes at 174 volts on the arc. To secure a relatively increased intensity of radiation in the 2537A line, Uviarcs may be immersed in water to various depths depending upon the effects desired. Depending upon the temperature, the arc voltage then does not rise to more than 20 to 40 volts at 4 to 5 amperes. Wood [127] made use of this method.

When so operated, the arc has the volt-ampere characteristic of a low-pressure arc, although the current density in the arc is greatly in excess of that obtainable

[127] Wood, R. W., *Phil. Mag.*, **50**, 761 (1925); compare also Taylor, H. S., *J. Am. Chem. Soc.*, **48**, 2480 (1926).

under conditions of temperature equilibrium in open air. This is an inefficient operating condition. The inlead wires are not intended to carry the excessive currents which may pass. Spattering from the tungsten anode is also greater than during operation at the same current and higher vapor pressures.

It is clear that the arc voltage drop depends upon the vapor pressure of the mercury, the mean vapor density of which increases with the temperature. The Uviarc dissipates about 50 watts per square inch of its silica tube, its mean temperature is about 360°C., and the vapor pressure about 800 mm. These are maximum ratings based on an economic life of 6000 hours of continuous operation.

Among the first thorough studies of the static characteristic curves of the mercury arc were those of Harrison and Forbes,[128] who clearly appreciated the possibility of following changes in voltage with constant current by altering the ventilation of the arc. They also showed the negative characteristic in certain regions of the static curve; an increase in applied voltage produces a decrease in the current. When it gets too hot the lamp goes out.

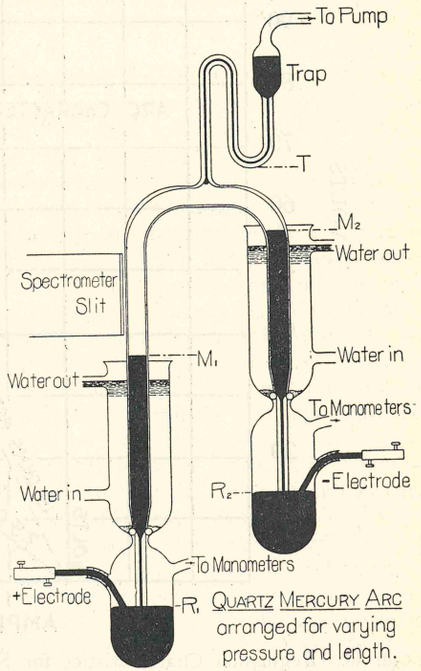


FIGURE 39.

Special Design of the Harrison and Forbes Experimental Mercury Arc (*Journal of the Optical Society of America*).

For their work on the influence of current and voltage on the spectral distributions of the radiations, they designed a special lamp with variable length. (Figure 39.) The results were reduced to unit length after deducting the electrode drop in voltage, taken as 12 volts. Legs of an inverted copper U dipped into two Pyrex reservoirs, sealed to them by de Khotinsky cement, the upper part of each serving as water-cooler and the lower containing mercury for the arc. Iron wires sealed into the sides of the reservoirs dipped almost to the bottom of the mercury pools. A quartz trap was sealed to the top of the arc, so that the last traces of air in the tube could be exhausted by boiling the

[128] Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, **10**, 1 (1925).

mercury up into the trap. When the lower legs and trap tube were of large bore, the arc had a great tendency to oscillate, the mercury levels moving up and down several centimeters and the arc-voltage varying by 20 per cent or more. To damp the oscillations down to a few hundredths of a millimeter and to keep the voltage constant, these legs were replaced below the water-coolers by quartz capillaries of 1 mm. internal diameter, the finest thread of mercury that would carry the maximum current of 5 amperes.

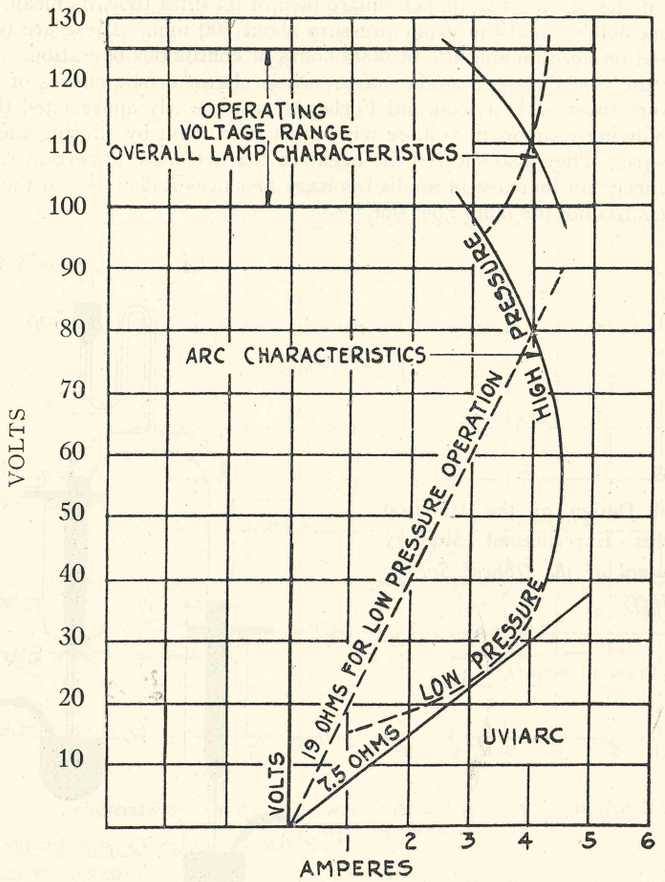


FIGURE 40. Regulation Characteristics for Slow Changes of Line Voltage (Buttolph, *Review of Scientific Instruments*).

The bands of the upper part of the tube were made with thickened walls to prevent fusion under the greater heat caused by deflected ions. The two reservoirs and trap were connected to vacuum through rubber pressure tubing by stopcocks, so that any one could be separately exhausted either through an inch of thermometer capillary or through a tube of large bore. Exact control of all mercury levels was possible. Air pressure up to two atmospheres could also be supplied to the reservoirs. Their pressures could be read from manometers.

In starting, both reservoirs and the body of the lamp were exhausted to a fraction of a millimeter and then mercury was allowed to rise slowly in the arms. The outside

of the lamp was heated by a Bunsen burner and the mercury boiled vigorously. When it had risen so as to fill partly the trap, the rubber tube connecting this to the pump was closed with a pinch-cock as near the trap as possible. The current was then turned on, the upper electrode being negative. The two reservoirs were then slowly exhausted until the mercury broke at the top of the U, and the arc length then increased as the pressure was built up in the tube. The height of the mercury columns was finally adjusted by varying the resistance in series with the lamp, the rate of cooling, and the pressure in the two reservoirs. Although the upper reservoir gradually filled at the expense of the lower, the excess could be returned without extinguishing the arc. A copper tube with small holes was bent to the shape of the quartz tube and air currents were directed on the whole luminous column when necessary. With this apparatus, a change could be made from one stationary state to another on a different characteristic curve much more rapidly than in the ordinary arc. The pressure could be built up rapidly in the arc when first struck by lengthening it to 25 cm., putting a large current through it, and then shortening the column, thus building up the voltage drop. The whole arc was enclosed in a large box with holes to provide variable degrees of ventilation. In series with the arc was a fairly high inductance to damp out oscillations and a variable maximum resistance of 200 ohms capable of carrying 5 amperes. The arc was fed by a 550-volt direct current generator, run on an induction motor. In no case was the voltage drop across the arc greater than 300 volts, or 17 volts per centimeter. Langmuir[129] also developed a cooled arc for the study of the characteristics of arcs at different vapor pressures.

By combining the "static" characteristic of the arc (H-L, Figure 37) with the volt-ampere characteristic of the fixed series resistance to be employed with it, there is obtained the volt-ampere curve of the actual working combination, shown in full lines in Figure 40. The use of greatly increased resistance to secure low pressure operation of the Uviarc is also shown in broken lines. The curved line marked "high pressure" is the supply voltage less the voltage drop in the series resistance and so represents the voltage available for operation of the arc at various stable arc currents. For the arc to be stable, the slope of this curve must be such that for various line voltages the voltage available for arc operation is never less than the arc drop. Buttolph emphasizes that the arc voltage is related to the current only indirectly through its ability to change the temperature and therefore the vapor pressure of the mercury. The positive volt-ampere characteristic of the Uviarc secures good "regulation" (change of voltage with current) only for very slow changes in the supply voltage which permit the attainment of temperature equilibrium.

The practical stability characteristic of the arc is better indicated by a family of "dynamic" regulation curves, such as are indicated by the series of arrow-marked lines of Figure 41. This shows the effect of sudden changes in supply voltage so rapid as to make the immediate effect of temperature changes negligible. The arrow-marked lines show approximately what happens as a result of sudden changes in supply voltage to new voltages maintained until temperature equilibrium has been attained. Since the apparent resistance can change only with the vapor pressure, the first effect of an increase in the supply voltage is only an increase in the arc current. With the resulting temperature increase, the arc voltage increases, the series resistance voltage decreases, the current decreases and normal operation is resumed at a higher arc voltage with practically the original current. A sudden change back to the normal and original voltage results in a completion of the cycle in a manner identical with that indicated for sudden decreases from normal. For transient voltage fluctuations, this cycle becomes greatly distorted and at high frequencies finally degenerates to changes only along the line LNH. The fact that the Uviarc current only affects the arc voltage rather slowly through the arc tempera-

[129] Langmuir, I., *Gen. Electric Review*, **27**, 538 (1924).

ture, affects its apparent static instability, the cycle shown by the lines L'N'H' requiring a relatively long time for completion. The curve marked "arc watts" shows that a condition of energy and temperature maximum exists at approximately the normal operating voltage. The "regulation" of the lamp depends upon the amount of series resistance used; this is determined by the permissible arc current fluctuation and the local variation in power supply voltage.

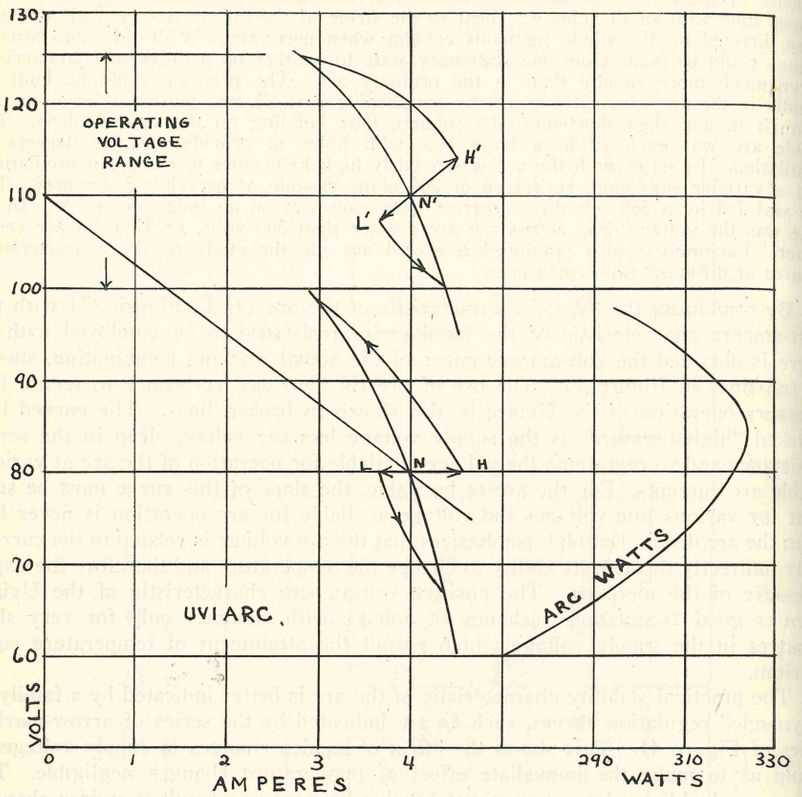


FIGURE 41. Regulation Characteristics for Sudden Changes of Line Voltage (Modified from Buttolph, *Review of Scientific Instruments*).

There is also an inherent instability of the arc, related to changes in its apparent resistance, and ascribed to transient high-frequency variations of the current. This appears to be a cathode phenomenon, the cause of which is not definitely known. These current variations are most pronounced during low-pressure operation at starting and result in an arc-extinguishing effect opposed only by the impedance of the circuit. The arc and its supply line act much like a series resonant circuit. The frequency of the oscillations may be several thousand per second; several thousand volts may be induced on the arc terminals, resulting in transient reductions of the current to amounts insufficient to maintain the arc. This form of instability may be largely eliminated by inserting sufficient resistance to absorb one-third of the

supply voltage. In practice, one-quarter henry (or for a very unstable direct-current supply line or for rectifiers with pulsating output, one-half henry) in an open-core inductance connected in series with the arc and as directly as possible to the cathode, permits stable operation with about 10 per cent greater voltage on the arc than would otherwise be possible.

The arc is essentially a direct current device because the cathode cannot be maintained active on alternating current half-time operation. It may, however, be operated upon alternating current by using a rectifier circuit and an arc with two anodes. (See Figure 42.) The cathode is connected to the secondary midpoint of a transformer, and the anodes are connected to its terminals. The series resistance may be in two sections placed adjacent to the anodes, or in a single unit placed either between the arc cathode and the transformer or in series with the primary. Either the anodic or the primary positions are preferable. The mercury cathode remains continually negative relative to either one anode or the other at all times,

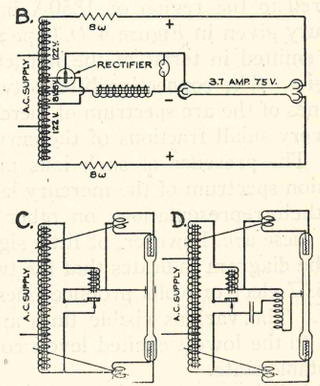


FIGURE 42.

Circuits for Alternating Current Mercury Arc (Buttolph, *Transactions Illuminating Engineering Society*).

being maintained through zero supply voltage by the cathode inductance. The electron stream passes from the cathode to one anode during the active half-cycle, to the other anode during the following half-cycle, and to both anodes during the transition. The inductance has the new function of maintaining the arc current at a level sufficient to keep the hot spot alive during zero voltage. This effect can be secured by using a transformer of sufficient magnetic leakage and even the regulating resistance can be replaced by reactance, but either of these changes causes so great a lowering of the power factor as to be impracticable. Buttolph[130] gives a detailed analysis of typical oscillograms, which lies beyond the scope of this book.

The starting of the alternating-current arc is complicated by the fact that the starting circuit is, in effect, connected to but one of the two anodes, and that the current flowing in the shifter circuit is alternating and hence is of the correct polarity for arc starting but one half of the time. A further limitation to the use of this method in the starting of the alternating-current rectifier type of arc lies in the fact that to secure a satisfactorily high induced potential, the negative inductance or choke must be of so high a value that a potential of about 120 volts must be applied to the starting circuit in order to secure a satisfactory shifter current. This causes great stability in the shifter arc, resulting in a trailing of the shifter arc through to the extreme end of the half cycle in which the mechanical break occurs. Figure 42B shows a solution of several of these problems[131] through the use of a small dry rectifier supplying about one ampere of

[130] Buttolph, L. J., *Rev. Sci. Instruments*, **1**, 500 (1930).
[131] Buttolph, L. J., *Trans. Illum. Eng. Soc.*, **28**, 153 (1932).

rectified direct current of just sufficient voltage to cause a flow of about one ampere through the inductance. The impedance of even one-third henry choke to this pulsating direct current is so low that the equivalent of only about a three- or four-volt direct current supply is required to secure a shifter current of over one ampere.

Other starting methods as a choke and either a mercury switch or a mechanically operated circuit-breaker may be used to secure high voltage transients sufficient to ionize the gas and start the discharge in the ordinary type of alternating current arc. (Figure 42C.) An alternative to the relatively slow action of a mercury interrupter or of a mechanically vibrating interrupter is the use of a simple oscillatory circuit (Figure 42D) in which there is imposed on the arc tube a high-voltage, high-frequency impulse, the high-frequency nature of the discharge being effective through the use of an external electrode placed preferably somewhere near the center of the arc tube.

A detailed treatment, based upon studies with the oscillograph, has been given by Buttolph and Dana.[132]

The Mechanism of the Emission of Radiation

The radiation emitted by the Uviarc extends from the 10,140A [133] line in the infrared to the region of 1850A in the ultraviolet. The energy-level diagram of mercury given in Figure 4 (Chapter 2) forms the basis for an interpretation of the lines emitted in terms of the impacts of electrons possessing the necessary kinetic energies. The connecting lines between the various energy states represent most of the lines of the arc spectrum of mercury. It has been stated in the preceding section that very small fractions of the current are carried by ions of valence higher than one. The presence of such ions makes it possible that some of the lines of the emission spectrum of the mercury lamp may be ascribed to transitions which would find their representations on other energy level diagrams for the corresponding ions; these are, however, of little significance.

The diagram indicates that the two resonance states produced by impacts of 4.87 and 6.67 electron-volts produce lines in the ultraviolet at 2537 and 1849A, respectively. The various visible lines are produced by transitions from higher energy levels to the lowest excited levels corresponding to the resonance potentials or to a metastable state.

The metastable states of the mercury atom are energy levels from which there occur no transitions with emission. The diagram indicates that 7.7 volts (applied in two stages) produces an energy level 2^3S_1, from which the green line 5461A is emitted, the atom falling into a metastable state, 2^3P_2. A second metastable state, 2^3P_0, is produced similarly by a transition from the 2^3S_1 state with emission of the 4047A line. While the usual higher energy level states have a duration of about 10^{-8} second, the metastable states persist for times of the order of 10^{-3} to 10^{-4} second.[134] The metastable states can also be reached from the normal states by direct electron impacts, but the direct transition from a metastable to a normal state is very improbable, so much so that the lines corresponding to such transitions are "forbidden" lines. Various processes limit the existence of an atom in a metastable state. Another electron can hit it and raise it to a higher energy level or even ionize it. It may suffer impact with another atom and gain or lose energy thereby. In the presence of a gas with a lower resonance or ionization potential, the metastable atom may yield some of its energy to one of the foreign atoms, raising it to a higher energy level or ionizing it.

[132] Buttolph, L. J., and Dana, D. W., *Rev. Sci. Instruments*, **4**, 209 (1933). Note also Kelting, R. C., U. S. P. 2,152,998, Apr. 4, 1939.

[133] For the infrared arc spectrum of mercury, see Wiedermann, G., and Schmidt, W., *Z. Physik*, **106**, 273 (1937); Murakawa, K., *Z. Physik*, **108**, 168 (1938).

[134] Methods for the determination of these life periods for various energy level states lie beyond the scope of this book. See Mitchell, A. C. G., and Zemansky, M. W., "Resonance Radiation and Excited Atoms," Cambridge, 1934.

Since in the operation of the usual forms of the mercury arc all the arc lines are emitted in addition to the resonance lines, the conditions must be such as to enable the bombarding electrons to raise the mercury atoms to the energy level corresponding to the ionization potential of 10.4 volts, although the voltage drop at the cathode by which the electrons are accelerated is only about 10 volts. Compton [135] suggested that the ionization must be produced as a result of two impacts. The electron energy is close to that required for the production of metastable atoms (see Figure 4) or to ionize these when formed.

The intensity of a line depends upon the fraction of the atoms in process of transition from a higher to a lower state; this depends upon the concentration of higher state atoms. This in turn varies directly with the electron current and the concentration of the atoms in the lower state, that is, with the current and pressure. Furthermore, the velocity of the electron must be sufficient to effect the transition in question; this depends on the voltage gradient in the region in which the electron acquires its velocity. For forming the 2^1P_1 state of mercury (6.67 volts), the probability of excitation increases from zero at 6.67 volts to a maximum at 6.8 volts, after which it decreases.[136] Similar considerations apply to each of the other states; the varying probabilities of excitation to each of these states under operating conditions accounts for the varying intensities of the lines which correspond to transitions from these states.

The theory is, however, much more complex, since the intensity of a line depends not only on the probability of formation of the necessary energy state, but also upon the probability of the transition from that state. This is true since other transitions from that state producing other lines may also occur. In place of dropping to one of several lower excitation states with emission of the corresponding lines, it may also be raised to a still higher state of excitation by suffering impact with an electron. The further analysis of these probabilities of emission, collision or ionization depends upon the determination of the mean free paths of the atoms and of their effective radii for collisions.

The uniformity of the light emitted along the lengths of the positive column shows that the electrons must acquire energy from some source other than the cathode fall. It comes from the energy input into the column, the product of the arc current into the voltage gradient. The latter factor depends upon the current density and the pressure. Schottky [137] believed the voltage gradient to vary inversely with the tube diameter. For mercury vapor, Güntherschulze [138] found at different pressures that the gradient is a function of the tube diameter, d, and the current I, $X = \frac{c}{d^a I^b}$, a, b, and c being constants. The values of a and b vary with the pressure of the mercury vapor. At 100°C., a is 0.69 and b is 0.12.

Within the positive column, the average kinetic energy of the electrons is too low to excite or ionize the mercury atoms. There is, however, a Maxwellian distribution of the kinetic energy among the electrons, so that a small fraction of them do have a sufficient amount of energy to produce these effects. The average kinetic

[135] Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931); see also Mason, R. C., *Phys. Rev.*, **38**, 427 (1931); Gehrts, A., and Vatter, H., *Z. Physik*, **79**, 421 (1932); Barnes, B. T., and Adams, E. Q., *Phys. Rev.*, **53**, 545, 556 (1938); Fabrikant, V. A., Butaeva, F., and Tsirg, *Physik. Z., Sowjetunion*, **13**, 23 (1938); *Chem. Abs.*, **31**, 8352 (1937); **32**, 4871 (1938).

[136] Brattain, W. H., *Phys. Rev.*, **34**, 474 (1929).

[137] Schottky, W., *Physik. Z.*, **25**, 342, 635 (1924).

[138] Güntherschulze, A., *Z. Physik*, **41**, 718 (1927); **42**, 763 (1927) (glow discharge). See also Elenbaas, W., *Physica*, **5**, 568 (1938); *Chem. Abs.*, **32**, 7340 (1938).

energy ($3/2\ kT_e$) depends upon the electron temperature T_e. Killian [139] studied the effects of pressure upon the electron temperature and total electron concentration over a low pressure range in a mercury arc in a tube of 6.2 cm. diameter, carrying a current of 5 amperes. The electron temperature decreased from 38,000°K. at 0.00020 mm. to 19,900°K. at 0.00533 mm. An electron temperature of 19,900° means that the average kinetic energy of the electrons is 2.56 volts. The fraction of the electrons having kinetic energies greater than the ionization potential of mercury is in this case, from the Maxwell-Boltzmann distribution law, about 0.003.[140] The energy lost by this small fraction of the electrons in ionizing collisions is supplied by the energy input into the positive column. Killian found also that an increase in pressure increased the probability of collisions, although it reduced the electron temperature. These opposing effects cause the emission at constant current density to pass through a maximum as the pressure is increased. Other observations showed that the electron temperature tends to decrease somewhat with an increase in the arc current. In Killian's experiments, the average electron concentrations varied between 3.7×10^{10} and 15.2×10^{10} per cubic centimeter as the pressure was increased from 0.00020 mm. to 0.00533 mm. The theory of Tonks and Langmuir[141] indicates that there is also a concentration gradient for electrons from a maximum along the axis of the tube toward the walls. Not all of the energy input into the positive column is utilized in excitation or ionization. Some of the energy is delivered to the walls, being liberated there by the recombination of electrons and ions. As the electron temperature was decreased from 38000°K. to 19,900°K. in the experiments of Killian the energy delivered to the walls by recombination processes could be calculated to decrease from 48 to 14 per cent of the total input. The remainder was available for excitation processes.

These experiments do not apply directly to the usual types of mercury arc, since the pressure range is quite different. Lübcke [142] finds that the electron temperatures are 7000 to 40,000°K. in the more usual forms.[143]

Continuous and Band Spectra in the Mercury Arc

The line spectrum of mercury is superposed upon a fainter continuous spectrum, emitted by glowing vapor distilling from the arc. It has been in part attributed to incandescence. The continuous spectrum, together with the selective absorption of the luminous mercury vapor for its own radiation, in part accounts for a shift in the relative radiation intensity toward the longer wave-lengths with increased energy input, in contrast with Wien's displacement law. A review of continuous emission spectra in general has been given by Finkelnburg.[144]

Volkringer [145] observed a large band at 3360A and a smaller one with a maximum at 2650A. Dawson and Crew [146] found band maxima in the arc at atmospheric pressure, excited by high voltage and low current density, at 4500, 3300 and 2550A. No continuous radiation was emitted in the region 2535 to 2350A. On increasing

[139] Killian, T. J., *Phys. Rev.*, **35**, 1238 (1930).

[140] For further details of such calculations, see Dushman, S., *Elec. Eng.*, **53**, 1204, 1283 (1934).

[141] Tonks, L., and Langmuir, I., *Phys. Rev.*, **34**, 876 (1929).

[142] Lübcke, C., *Z. tech. Physik*, **14**, 298 (1933).

[143] For further details of probe tests in various mercury arcs, see Lübcke, C., *Z. tech. Physik*, **8**, 445 (1927); Gvozdover, S. D., and Konovalov, F., *Compt. rend. acad. Sci. U.R.S.S.*, **1**, 553 (1934); *Chem. Abs.*, **28**, 4975 (1934); Togo, S., *J. Inst. Elec. Eng. Japan*, **53**, 109 (1933); Klyarfel'd, B., and Plokhotzkii, E., *Z. tech. Physik (U.S.S.R.)*, **5**, 796 (1934); *Chem. Abs.*, **29**, 673 (1935).

[144] Finkelnburg, W., *Physik. Z.*, **31**, 1 (1930). See also Rompe, R., Schulz, P., and Thouret, W., *Z. Physik*, **112**, 369 (1939); Unsöld, A., *Ann. Physik*, **33**, 607 (1938).

[145] Volkringer, H., *Compt. rend.*, **185**, 60 (1927).

[146] Dawson, L. H., and Crew, W. H., *J. Opt. Soc. Am.*, **17**, 261 (1928).

the current, the bands broadened in both directions and filled this gap. Crew and Thornton [147] attribute the bands to the Hg_2 molecule produced at the distilling surface of the mercury and readily dissociated even by slowly moving electrons or ions. From the intensity of the band at 2540A at various temperatures and pressures, Koernicke [148] calculated the heat of dissociation of the molecule to be 1.4 kcal. Nakamura [149] regarded the 2536A band as due to the arc type of excitation of the neutral molecule and the band at 2540A as due to the ionized molecule Hg_2^+.[150]

[147] Crew, W. H., and Thornton, W. N., *J. Opt. Soc. Am.*, **19**, 358 (1929).

[148] Koernicke, E., *Z. Physik*, **33**, 219 (1925).

[149] Nakamura, G., *Mem. Coll. Sci. Kyoto*, **10**, 1 (1926); *Chem. Abs.*, **21**, 1755 (1927).

[150] For recent studies of the origin of the mercury bands, see Lord Rayleigh, *Nature*, **119**, 423, 778 (1927); **127**, 125, 854 (1931); *Proc. Roy. Soc.* **116A**, 702 (1927); **119A**, 349 (1928); Kuhn, H., *Naturwiss.*, **16**, 352 (1928); *Z. Physik*, **72**, 462 (1931); Ponte, M., *Compt. rend.* **186**, 633 (1928); Winans, J., *Nature*, **121**, 863 (1928); Pienkowski, S., *Bull. intern. Acad. Polonaise*, Nos. 4-5A, 171 (1928); *Chem. Abs.*, **23**, 2103 (1929); Dziedzicki, N., *Compt. rend. soc. polonaise Phys.*, **3**, 207 (1928); *Chem. Abs.*, **23**, 5095 (1929); Hulubei, H., *Compt. rend.*, **193**, 154 (1931); Hamada, H., *Phil. Mag.*, **12**, 50 (1931); Winans, J., *Phys. Rev.*, **37**, 897, 902 (1931); **39**, 745 (1932); **42**, 800 (1932); Okubo, J., and Matsuyama, E., *Nature*, **129**, 653 (1932); *Science Repts. Tohoku Imp. Univ., 1st series*, **22**, 383 (1933); *Chem. Abs.*, **27**, 5642 (1933).

Chapter 7

Output of the Mercury-vapor Lamp Under Various Operating Conditions

Methods of Measuring the Intensity of the Radiations

The evaluation in absolute energy units of the radiations in various lines or wave-length regions emitted by a radiation source is difficult and requires means for the isolation of various wave-length bands by filters or monochromators as well as means for measuring the energies radiated within these bands. To avoid the difficulties involved and the apparatus required for such measurements a number of workers have described photochemical reactions which indicate the effectiveness of a radiation source for conducting photochemical changes. Many of these reactions are of little value, and even the better ones require a critical understanding of all the physical factors involved if they are to be employed effectively.

Among the apparati used for measuring the quantity of radiant energy are thermopiles. When it is desired to express the results in absolute units of energy, the thermopiles must be calibrated against some standard source of energy. Thermopiles are non-selective and measure radiant energy of any wave-length. Their use is described in the following references, those by Coblentz giving detailed directions [1] for the construction, installation and use of these instruments. More recent descriptions have been given by Strong [2] and Cartwright [3]; precautions in the use of these instruments have been given by Leighton and Leighton.[4]

Mere exposure of a thermopile to a source gives information only as to the total energy emitted, but tells nothing of the distribution of radiations among the various spectral regions. To measure distribution in the ultraviolet region a quartz monochromator, by means of which the wave-lengths can be separated into very narrow bands, is frequently employed with the thermopile.[5] When using thermopiles with quartz monochromators, correction should be made for slit width,[6] aberrations, reflection, absorption, and scattering in the optical train. McAlister [7] has described in detail the use of two quartz monochromators for determining absolute ultraviolet intensities by the aid of vacuum thermopiles and Photronic cells.

It is possible, however, to obtain information regarding the spectral distribution

[1] Coblentz, W. W., *Bur. Standards Bull.* **4,** 391 (1908); **9,** 7 (1913); Moll, W. J., and Burger, H. C., *Z. Physik,* **32,** 575 (1925); Coblentz, W. W., *J. Opt. Soc. Am.,* **5,** 259 (1921); Voege, W., *Physik. Z.,* **22,** 119 (1921).

[2] Strong, J., *Rev. Sci. Instruments,* **3,** 65 (1932).

[3] Cartwright, C. H., *Rev. Sci. Instruments,* **3,** 73 (1932).

[4] Leighton, P. A., and Leighton, W. G., *J. Phys. Chem.,* **36,** 1882 (1932).

[5] For a critical discussion, see Forbes, G. S., Report of the Committee on Photochemistry of the Division of Chemistry and Chemical Technology of the National Research Council, *J. Phys. Chem.,* **32,** 491 (1928).

[6] Coblentz, W. W., Dorcas, M. J., and Hughes, C. W., *Bur. Standards Sci. Paper,* **21,** 535 (1927); Coblentz, W. W., *Bur. Standards Bull.* **10,** 41 (1914); **17,** 1 (1920); Franklin, R. G., Maddison, R., and Reeve, L., *J. Phys. Chem.,* **29,** 713 (1925).

[7] McAlister, E. D., *Smithsonian Miscellaneous Collections,* **87,** No. 17 (1933).

of the energy emitted by a source, by employing filters for delimiting various ultraviolet regions.[8] Such methods are illustrated in the work of Gillam and Morton discussed below in connection with chemical actinometers. Stockbarger and Burns [9] have reported methods for standardization of the conditions to be met in the use of filters, which methods are discussed in more detail in Chapter 10. In general, the infrared energy, the energy in successively shorter-wave regions of the visible and the energy in the ultraviolet range are measured in successive experiments with the corresponding filters. The energy introduced in each of the increments is calculated by differences. The equivalent wave-length range of the increments is approximated from the filter transmission curves.[10] Fabry and Buisson [11] measured the total energy L transmitted by n different filters, of thickness d (or n different thicknesses of the same filter). They solved n equations of the form $L = A_1 e^{-m_1 d}$, ... $A_n e^{-m_n d}$ for $A_1 .. A_n$, the n monochromatic intensities of the original source; $m_1 .... m_n$ were determined separately for each filter.[12]

Also, photoelectric cells have been used for energy measurements. Such cells have almost linear intensity-current curves, and are free from time-lag, fatigue and deterioration. Their use, however, requires a knowledge of the sensitivity regions of the various cells, since these cells are selective in their response to particular wave-length regions. When the measurement is intended to serve as an indication of the suitability of a source for effecting a given photochemical change, the wave-length region necessary to bring about the reaction must be known in order that the appropriate photo-cell may be selected.

Elster and Geitel [13] used a zinc sphere for measuring ultraviolet radiation through photoelectric effect. Szillard used cadmium in the cathode of a photoelectric cell sensitive to the region 2950 to 3900A. Griffith,[14] by employing a quartz window to the above cell, made it sensitive to 2000A and with Taylor [15] adapted it to the photometry of therapeutic lamps. Harris [16] replaced the electrometer or gold-leaf electroscope used in conjunction with such cells by more robust measuring apparatus. He adapted a thermionic valve and microammeter to a circuit employed for the measurement of the output of a quartz mercury arc. Miethe and Stenger [17] used a silver film, and Anderson [18] has described a method of measuring and controlling the total ultraviolet output from a quartz mercury arc by using the Weston "Photronic" light-sensitive cell.

An ultraviolet light meter described by Rentschler [19] comprises special uranium, thorium, cerium, titanium and tantalum photoelectric cells connected to a glow relay tube. The latter consists of an iron cathode, a thorium starting anode and a main anode contained in an inert gas atmosphere. The intensity of incident radiations is proportional to the rate at which an electromechanical counter actuated by the glow tube registers. The total energy is measured by a recording

[8] See Krefft, H., and Rössler, F., *Z. tech. Physik,* **17,** 479 (1936).

[9] Stockbarger, D. C., and Burns, L., *Phys. Rev.,* **34,** 1263 (1929).

[10] Coblentz, W. W., Long, M. B., and Kahler, H., *Bureau of Standards Bull.* **15,** No. S 330 (1918).

[11] Fabry, C., and Buisson, H., *Compt. rend.,* **152,** 1839 (1911).

[12] Coblentz, W. W., and Kahler, H., *Bur. Standards Bull.* No. 378 (1920). Ornstein, L. S., *J. phys. radium (7),* **4,** 613 (1933). Kawa, J., *Towarzystwa Fiz.,* **4,** 27; *Chem. Abs.,* **25,** 2361 (1931).

[13] Elster, J., and Geitel, H., *Physik. Z.,* **12,** 609 (1911); **13,** 739, 852 (1912).

[14] Griffith, H. D., *Lancet,* 5th December, 1205, 1925.

[15] Griffith, H. D., and Taylor, J. S., *J. Hyg.,* **25,** 218 (1926).

[16] Harris, D. T., *J. Sci. Instruments,* **6,** 2 (1929).

[17] Miethe, A., and Stenger, E., *Z. wiss. Phot.,* **19,** 57 (1919).

[18] Anderson, W. T., Jr., *Rev. Sci. Instruments,* **5,** 127 (1934).

[19] Rentschler, H. C., *J. Am. Inst. Elec. Eng.,* **49,** 113 (1930); see also U. S. P. 1,923,844, August 22, 1933.

meter. Cerium is photo active below 4500A, thorium below 3700A, uranium below 3200A, titanium between 2700-3200A, and tantalum between 2000-3000A. A proper choice of metal and quartz or glass container allows radiations of definite wave-length bands to be measured. It has been employed, with some modifications, in the investigations on air pollution conducted at the Mellon Institute.[20] Figure 43 shows the wiring diagram of the Rentschler Ultraviolet Meter.[21] The photoelectric cell shown on the central panel is mounted in a special glass bulb which admits all the ultraviolet reaching the surface of the earth. It has two electrodes, a central rod and a cathode of uranium, sputtered (in argon) over a small area of approximately 12 square centimeters on the inside wall of the bulb.

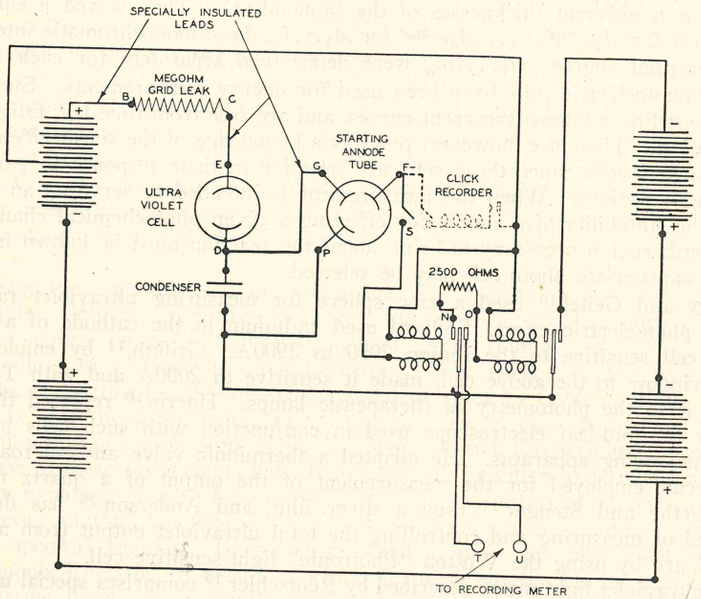


FIGURE 43. Wiring Diagram for Ultraviolet Meter (Meller, Hibben and Warga, *Transactions Illuminating Engineering Society*).

The uranium cathode, by emitting electrons, allows current to flow through the cell only when radiations between 2700 and 3350A fall upon it. The current is proportional to the intensity of the radiation, but is very small (0.1 microampere) and requires amplification by a glow relay or starting anode tube. The current trickling through the cell slowly charges a condenser. When this reaches a fixed value, the condenser spills over and an impulse of current flows between its plates. The frequency with which this occurs is proportional to the intensity of the radiation. The current flow in the tube at this point operates either a click recorder or a graphic recording meter in which a moving pen integrates the impulses over

[20] Meller, H. B., Hibben, S. G., and Warga, M. E., *Trans. Ill. Eng. Soc.*, **27**, 64 (1932).

[21] Rentschler, H. C., and Henry, D. E., U. S. P. 1,815,073, July 21, 1931; British P. 353,981, June 12, 1929; Rentschler, H. C., U. S. P. 1,871,280, Aug. 9, 1932; 1,917,854, July 11, 1933; British P. 353,554 and 353,555. Special fluorescent filters for use in conjunction with such photocells have been described by E. D. Wilson, U. S. P. 2,128,110, Aug. 23, 1938; *Chem. Abs.*, **32**, 7824 (1938).

a short time interval. The record discloses variations that may occur rapidly. The sensitivity of the uranium photo-cell, shown in Figure 44, is at a maximum between 2950 and 3000A. Different cells have different sensitivities and each cell must be calibrated. According to Meller, Hibben and Warga, the chief source of error is leakage to the ground or around the condenser. They calibrated their meter against a standard tungsten-ribbon lamp which, operated at 27.5 amperes, had a true temperature of 2800°K. The results are given in arbitrary units, the number of impulses per unit of time.

Dorno [22] also finds the cadmium cell to be sensitive between 2800 and 3500A. Coblentz and Stair [23] described a portable ultraviolet intensity meter comprising a photoelectric cell, balanced amplifier, and microammeter.[24] Coblentz [25] developed a practical field method for determining the energy distribution of the sun in absolute units. Two methods were devised, one employing filters and a balanced thermopile calibrated in absolute value against a standard of thermal radiation. The other employed a titanium photoelectric cell calibrated in absolute value against a standard of ultraviolet radiation. For the latter, Coblentz and Stair [26] use a commercial vertical mercury-in-quartz arc.[27] It proved of especial value

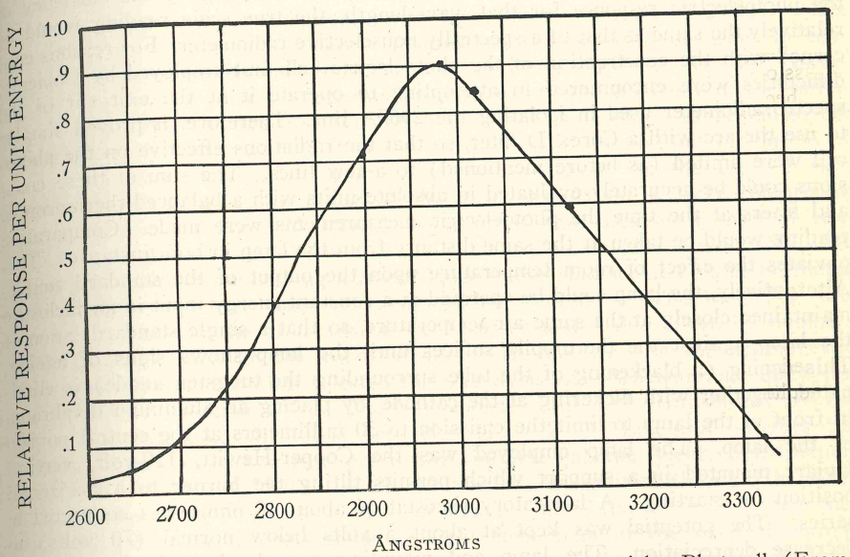


FIGURE 44. The Response or Sensitivity Curve of the Ultraviolet Photocell (From Meller, Hibben, and Warga, *Transactions of Illuminating Engineering Society*).

[22] Dorno, C., *Strahlentherapie*, **25**, 361 (1928); *Chem. Abs.*, **22**, 1540 (1928).

[23] Coblentz, W. W., and Stair, R., *Bureau Standards J. Research*, **12**, 231 (1934).

[24] For further discussion of the calibration of photoelectric cells, or for the use of thermopiles and filters in measuring the energy distribution of sources, see Coblentz, W. W., *Science*, **76**, 412 (1932); *Strahlentherapie*, **50**, 179, 487 (1934); *Am. J. Roentgenol. Radium Therapy*, **33**, 793 (1935); Coblentz, W. W., Stair, R., and Hogue, J., *Bur. Stand. J. Res.*, **7**, 723 (1931); **8**, 759 (1932); Coblentz, W. W., *Bull. Bureau Stand.*, **9**, 51 (1912); **11**, 87; *Bur. Stand. J. Res.*, **11**, 79 (1933).

[25] Coblentz, W. W., *Puerto Rico J. Public Health Trop. Med.*, **11**, 1 (1935); *Chem. Abs.*, **30**, 118 (1936).

[26] Coblentz, W. W., and Stair, R., *J. Res. Bur. Standards*, **16**, 83 (1936).

[27] Report of the Illuminating Engineering Society Subcommittee on the Measurement of Ultraviolet Radiation, *Trans. Illum. Eng. Soc.*, **28**, 864 (1933).

as a standard for meters used to evaluate sources for germicidal and erythema-producing effects by the aid of the photo-cell. Since the cell is insensitive to wave-lengths longer than about 3300A, and since the short-wave response may be limited to about 2800A by enclosing the cell in Corex D glass, practically only the strong emission lines at 2967, 3024 and 3132A are effective. A gas-filled tungsten lamp has been employed occasionally as a standard, but a source emitting a continuous spectrum has several disadvantages over the discontinuous spectrum of the mercury arc.

One method of calibrating a photoelectric intensity meter in absolute values comprises observing the microammeter reading on exposure of the cell to a strong emission line of the mercury arc, *e.g.*, 2967A, the energy value of which had been determined in absolute units. By dividing the scale reading by the efficiency of the photoelectric response for that wave-length, the true scale reading would be relatively the same as that of a spectrally nonselective radiometer. For reasons concerned with the construction of the photoelectric cell first employed by Coblentz, difficulties were encountered in attempting to operate it at the exit slit of the spectroradiometer used in isolating the 2967A line. Therefore, it proved simpler to use the arc with a Corex D filter, so that the radiations effective on the photocell were limited (as before mentioned) to a few lines. The sum of these emissions could be accurately evaluated in absolute units with a balanced thermocouple and filters at the time the photoelectric measurements were made. Comparative reading would be taken at the same distance from the lamp in both instances. This obviates the effect of room temperature upon the output of the standard source. Alternatively, the lamp could be operated at a constant energy input in an inclosure maintained closely at the same air temperature, so that a single standardization of the lamp against the thermopile suffices until the lamp shows signs of ageing. This ageing (a blackening of the tube surrounding the tungsten anode) is eliminated, together with flickering at the cathode, by placing an aluminum diaphragm in front of the lamp to limit the emission to 30 millimeters at the central portion of the lamp. The lamp employed was the Cooper-Hewitt, 110-volt, vertical Uviarc mounted in a support which permits tilting the burner to a horizontal position for starting. A laboratory rheostat of about 18 ohms was connected in series. The potential was kept at about 5 volts below normal (70 volts) to decrease depreciation. The lamp and mounting may be kept in a ventilated, galvanized housing. When used with the diaphragm, the apparent depreciation is slow. Operated on a storage battery, the lamp remains constant at 65 ± 0.3 volts. This slow fluctuation of ± 0.3 volt is probably the result of changes in ventilation and is easily controlled with a rheostat, so that the ultraviolet output in a particular region is regulated within two or three parts in 1500.

Gyemant [28] described a fluorescent intensimeter for ultraviolet rays. A simple "UVscope" described by Alexander and referred to by Moss and Knapp was a filter of Chance's glass which absorbed all rays shorter than 3650A, the longer transmitted rays being recorded by their effects on photographic paper. The Hanovia Co.[29] described an apparatus with a fluorescent screen and ammeter indicator from which the intensity of the light could be directly read.

The Geiger-Müller electron counter, widely used in cosmic ray measurements, has been employed for the measurement of an ultraviolet beam, by counting the electrons produced by the photoelectric effect of the beam. The counter is used

[28] Gyemant, A., *J. Opt. Soc. Am.*, **12**, 65 (1926).

[29] Croad, A. K., British P. 320,794, Nov. 8, 1928, to The Hanovia Co.; *Brit. Chem. Abs.*, **B**, 1021 (1929).

chiefly in the study of ultraviolet of very low intensities, such as the assumed mitogenetic rays.[30]

Chemical Actinometers. Comparison of some chemical actinometers was given by Eidinow.[31] Since the reactions depend upon the intensity of restricted wave-length regions, the results of such measurements may show apparent disagreement. In using chemical methods as a rough guide to the times of exposure required for a given reaction to be effected by a lamp, it is essential to select a test reaction which is effected in approximately the same wave-length region as that required for the reaction to be conducted. This is true since every photochemical reaction has its own characteristic curve of spectral sensitivity, while every light source has its own spectral energy distribution. Thus for controlling the bactericidal action of a lamp, it is necessary to choose as a test reaction one which is not effected by visible radiations or by those longer than about 2950A. (See Chapter 35.) Dorcas and Forbes [32] pointed out the necessity of using in conjunction with a chemical actinometer, a filter which transmits for each wave-length a fraction of incident radiation proportional to the efficiency of the radiation in promoting the reaction for which the light is intended to be employed. This method of measurement furnishes a comparison of the abilities of sources of different spectral distribution to effect a given reaction. In the case of skin erythema tests, taken as an index of biological stimulation, a filter comprising a one-centimeter thickness of 0.00025 molar picric acid between a sheet of red-purple Corex glass 2.5 mm. thick and one of clear Corex was utilized. This filter had an absorption curve bearing a resemblance to the Hausser and Vahle erythema curve [33] replotted on the basis of quanta rather than ergs. The replotting was done by multiplying the ordinates of the Hausser and Vahle curve by numbers inversely proportional to the corresponding wave-lengths. As the actinometric reaction, Dorcas and Forbes selected the photolysis of *p*-benzoquinone in 50-per cent alcohol, a reaction which absorbs completely the light transmitted by the filter. This reaction, which had been studied by P. A. Leighton, satisfies the necessary condition of having a practically constant quantum yield (See Chapter 12) between 3130 and 2540A. Each wave-length transmitted through the filter may be assumed to photolyze a mass of quinone proportional to the erythema-producing power of the corresponding light component of the original source. The irradiation period was two hours. A second sample was kept in a dark vessel for the same period as control. Both samples were then cooled in ice, and titrated simultaneously with $0.004N$ thiosulfate, adding 10 cc. of normal iodide and of 1.5 normal hydrochloric acid at the start, with starch indicator. It was assumed that all of the monochromatic effects for this reaction could be integrated by summation since the reaction has no induction period and only a few per cent of the reaction material is decomposed, so that absorption by reaction products does not interfere. A plot of the milligrams of quinone decomposed per hour by a series of differently cored carbon arcs against the reciprocals of the times required for the production of a standard erythema indicated a fair degree of proportionality. As such proportionality implies that the reciprocity law holds for both reactions (erythema and photolysis), the slight variations from proportionality involving a

[30] Stoll, B., *Helv. Phys. Acta*, **8**, 3 (1935); Locher, G. L., *Phys. Rev.*, **42**, 525 (1932); Audubert, R., and Reithmuller, C., *Compt. rend.*, **200**, 389 (1935); Karev, M., and Rodionov, S., *Z. Physik*, **92**, 615 (1934); Audubert, R., and Mattler, J., *Compt. rend.*, **206**, 1005 (1938).

[31] Eidinow, A., *Lancet*, **209**, No. 5320 (1925).

[32] Dorcas, M. J., and Forbes, G. S., *J. Am. Chem. Soc.*, **49**, 3081 (1927).

[33] Hausser, K. W., and Vahle, W., *Strahlentherapie*, **13** (1923); see Chapter 36.

threshold intensity indicate that the reciprocity law does not hold exactly for the erythema reaction.

There had been many attempts to devise methods of chemical actinometry, usually with the object of measuring the value of a source for producing erythema, but rarely had the physical principles underlying the method been analyzed with such thoroughness. Filters were rarely applied (or were used only in a relatively crude manner) and reliance was placed instead upon the choice of a reaction which might be effected within the same wave-length range as that of the reaction to be studied, if, indeed, any consideration at all was given to the matter. The absorption curve of the actinometer was usually taken as an index to the wave-length region within which it is photochemically effected. Variations in the efficiency of the monochromatic rays within the absorbed band were disregarded, and the possibility of the occurrence of side reactions were not always eliminated.

Kistiakowsky and Heidt [34] point out that, although the errors of radiometric measurements can be estimated only by the original investigator, many difficulties may be avoided by the proper use of actinometry, and that, if later, the given actinometer is restandardized, it is easy to recalculate all quantum yields previously referred to it. They describe in detail an apparatus whereby the quantum yield of a photochemical gas reaction over any time interval during its course may be stated in terms of the quantum yield of uranyl oxalate decomposed by monochromatic light of the same wave-length with a probable error of 5 per cent.

Gillam and Morton,[35] among the earlier writers on actinometry, proposed the photochemical reduction of potassium nitrate to nitrite (determined colorimetrically) as an index of the bactericidal activity of a source. The absorption of light by nitrates commences at 3300A, rises to a maximum at 3000A, falls to a minimum at 2650 and rises very rapidly beyond this point. The quantum efficiencies below 2860A are, however, much greater than those in the region of selective absorption, so that despite the dissimilarity in absorption of potassium nitrate and bacteria, the photolysis in solutions buffered to pH 9.4 was held to resemble the bactericidal reaction in respect to the spectral distribution of photochemical efficiency.

By this method Gillam and Morton found that an unused mercury lamp gave nitrite equal to 6.4 cc. of N/5000 nitrite, while a used mercury lamp gave only 1.6 cc. An iron-nickel arc produced 5.2 cc. in one hour at 6 inches, or 1.3 cc. at 12 inches, so that the old mercury lamp and the metal arc were effective to roughly the same extent. A test showed that about 98 per cent of the nitrite formed by exposure to the unfiltered lamp owed its origin to rays on the short-wave side of the limiting ray (2750A) transmitted by 0.090 inch of a Vitaglass filter. This was held to indicate that the unfiltered reaction is applicable for measuring the relative bactericidal efficiency of different light sources. The unfiltered reaction is also suitable for indicating the deterioriation of a quartz lamp since this deterioration begins in the short-wave region to which the nitrate photolysis is sensitive. The reaction is, however, too slow for general use as a routine test for dosage in actinotherapy. It has been employed by Kestner [36] in comparing various ultraviolet sources.

Webster, Hill and Eidinow [37] found the bleaching of a solution of methylene-

[34] Kistiakowsky, G. B., and Heidt, L. J., *J. Am. Chem. Soc.*, **54**, 3246 (1932).
[35] Gillam, A. E., and Morton, R. A., *J. Soc. Chem. Ind.*, **46**, 417 (1927); see Chapter 20 for further discussion of the reaction.
[36] Kestner, O., *Strahlentherapie*, **46**, 574 (1933).
[37] Webster, T., Hill, L., and Eidinow, A., *Lancet*, **1924**, (1) 745.

blue in aqueous acetone to provide some guide to dosage in actinotherapy. The decomposition products of the acetone effect a bleaching of the dye which is proportional to the time of exposure, the dye evidently acting as a hydrogen acceptor.

Gillam and Morton [38] found by the use of filters that about 88 per cent of the acetone-methylene blue reaction is due to rays between 2000 and 2800A, 6 per cent to rays between 2800 and 3250A, and 6 per cent to rays on the long-wave side of 3250A. This indicates that the test is unsuitable as a criterion for the exposures required to effect the conversion of sterols to vitamin D (Chapter 39). On the other hand, it might serve as a simple means of determining dosages in bactericidal experiments. Moss and Knapp[39] criticized the test as lacking delicacy.

With mercury-vapor lamps at short distances the acetone-methylene blue test is fairly rapid. It is rather slow in sunlight, but for recording the ultraviolet intensity over a whole day this is an advantage. Exclusion of air is essential for securing reproducible results by this method.[40]

The uranium-sensitized decomposition of oxalic acid was employed by Freer and Gibbs [41] in studying solar radiation in the tropics and was applied to the determination of the intensities of the radiations from the mercury vapor arc by Mathews and Dewey.[42] The test was standardized for actinometry by Anderson and Robinson,[43] Leighton and Forbes,[44] and by Forbes, Kistiakowsky and Heidt.[45]

The spectrum of an oxalic acid-uranyl salt solution exhibits considerable absorption in the region between 3000 and 3800A. In agreement with this were the experiments of Gillam and Morton with filters of Vitaglass and window glass and a mercury arc, which indicated that 25-30 per cent of the decomposition of the oxalic acid-uranyl salt is due to rays on the long-wave side of 3250A and about 40 per cent to rays longer than 2800A. The region 2700 to 3250A appeared to account for about 20 per cent of the change. With the change induced by sunlight taken as 100, that through 0.09 inch of Vitaglass was 86.7, and through 0.105 inch window glass, 67.5. The test appears to indicate in a very rough way the intensity of those radiations effective in producing erythema. Moss and Knapp [46] thought the test to be a measure of the rather indefinite dye fading power of a lamp. 4 mm. of Pyrex transmits 40 per cent, 8.2 mm. of clear Corex 70 per cent and red purple Corex (10.2 mm.), 19 per cent of the total radiation as measured by this method.[47] Erythema on the upper arm is said to be produced by the same quantity of radiation which decomposes 0.056 mg. of oxalic acid per square centimeter in three minutes under standard conditions.

The "Uroxameter" of Moss and Knapp [48] is an elaboration of this test, using a specially designed vessel (made by Baird and Tatlock) rotated during irradiation of thirty minutes at a distance of 6.5 inches. The test solution consisted of a

[38] Gillam, A. E, and Morton, R. A., *J. Soc. Chem. Ind.*, **46**, 417 (1927).
[39] Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453 (1925).
[40] Osborn, T. W. B., and Stammers, A. D., *Brit. J. Actinotherapy*, **5**, 68 (1930).
[41] Freer, P. C., and Gibbs, H. D., *J. Phys. Chem.*, **16**, 709 (1912).
[42] Mathews, J. H., and Dewey, L. H., *J. Phys. Chem.*, **17**, 211 (1913).
[43] Anderson, W. T., Jr., and Robinson, F. W., *J. Am. Chem. Soc.*, **47**, 718 (1925).
[44] Leighton, P. A., and Forbes, G. S., *J. Am. Chem. Soc.*, **52**, 3139 (1930). In this paper the limitations of actinometry in polychromatic light are discussed.
[45] Forbes, G. S., Kistiakowsky, G. B., and Heidt, L. J., *J. Am. Chem. Soc.*, **54**, 3246 (1932). For a discussion of the reaction, see Chapter 24.
[46] Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453T (1925).
[47] Atkins, W. R. G., and Poole, H., *Sci. Proc. Roy. Dublin Soc.*, **19**, 355 (1929); *Brit. Chem. Abs.*, A, 1249 (1929).
[48] Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453T (1925); *Brit. J. Actinotherapy* (Jan., 1927).

mixture of 20 cc. of a 2-per cent aqueous solution of oxalic acid, 5 cc. of a 1-per cent solution of uranyl acetate in water, and 20 cc. of distilled water. For use with carbon arcs, an alternative stock solution richer in uranyl salt was recommended, and called the "20-strength" solution, since with it the distance of irradiation had to be greatly increased. The 20-strength solution was rather unstable, and had, according to Gillam and Morton, a somewhat different absorption spectrum than the normal mixture. Use of the stronger solution increases somewhat the values obtained through Vitaglass from a given source, the K.B.B. lamp. It was reported that a thickness of 2.2 mm. of the reacting solution absorbs all rays shorter than 3210A [49] and the method was said to indicate sensitivity to the region 3200-2300A. Brackett and Forbes [50] determined the gross quantum yields (see Chapter 12) at 21°C. (expressed as moles of oxalic acid per quantum) in a solution in which uranyl sulfate is 0.01 and oxalic acid 0.05 molar. The yields are 0.48 ± 0.01 at 2080A, 0.63 ± 0.03 at 2530A, and 0.59 ± 0.01 at 2780A. Forbes and Heidt [51] used uranyl oxalate rather than sulfate (.005 mole) and oxalic acid (.0025 mole) per liter. According to Pitzer, Gordon and Wilson [52] the rate of reduction of uranyl ion is small until just enough oxalic acid remains to form uranyl oxalate, when the rate of reduction rapidly increases. The presence of sulfuric acid has no effect on the relative rates. The photolyte in the actinometer is a complex, $H_2C_2O_4 \cdot UO_2C_2O_4$ which ionizes as a strong dibasic acid.

The hydrolysis of monochloracetic acid has also been employed in actinometry.[53] Bagnall [54] reports that the amount of iodine liberated from a solution of potassium iodide acidified with sulfuric acid is a measure of the chemical activity of sunlight and Rousseau [55] used this reaction in testing the permeability of various substances to the ultraviolet. Moss and Knapp [56] suggested that the reaction should be carried out in quartz vessels. They also pointed out that unless one unit of ultraviolet radiation liberates the same quantity of iodine from the nearly colorless potassium iodide solution as from the orange-colored mixture of solutions of iodine and potassium iodide, the quantity of iodine liberated will not be directly proportional to the amount of ultraviolet radiation incident upon the solution. Hymas [57] finds that for periods less than ten minutes, the amount of reaction is proportional to the energy absorbed. The potassium iodide-starch method has a temperature coefficient between 25° and 62°C. of -1.042 for ten degrees. He also finds the deterioration of a mercury lamp to be apparently greater when tested by its action upon potassium iodide than by its action upon sensitized oxalic acid.

From their studies of various methods, Gillam and Morton concluded that the nitrate and carbon tetrachloride methods are most suited to measure the bactericidal rays, while the three oxalic acid methods are more suitable for measuring the "middle ultraviolet."

Clark [58] employs the rate of darkening of zinc sulfide as a measure of ultraviolet intensity. Zinc sulfide and lithopone are sensitive from about 2500A to about 3600A,

[49] Moss, J. E., and Knapp, A. W., *Brit. J. Actinotherapy*, May, 1927.
[50] Brackett, F. P., Jr., and Forbes, G. S., *J. Am. Chem. Soc.*, **55**, 4459 (1933).
[51] Forbes, G. S., and Heidt, L. J., *J. Am. Chem. Soc.*, **56**, 2363 (1934).
[52] Pitzer, E. C., Gordon, N. E., and Wilson, D. A., *J. Am. Chem. Soc.*, **58**, 67 (1936).
[53] Dain, B., and Puzenkin, E., *Ber. Ukrain. wiss. Forsch. physikal. Chem.*, **4**, 75 (1935); *Brit. Chem. Abs.*, **A**, 1211 (1935); *Chem. Abs.*, **29**, 2451 (1935).
[54] Bagnall, H. H., *Analyst*, **54**, 101 (1929).
[55] Rousseau, E., *Compt. rend. soc. biol.*, **93**, 1480, 1482 (1925).
[56] Moss, J. E., and Knapp, A. W., *Analyst*, **54**, 334 (1929).
[57] Hymas, F. C., *Quart. J. Pharm.*, **2**, 281 (1929).
[58] Clark, J., *Am. J. Physiol.*, **69**, 900 (1924); *Am. J. Hygiene*, **9**, 646 (1929); *J. Opt. Soc. Am.*, **21**, 240 (1931).

with a maximum darkening at about 3200A. Mayerson [59] finds the method satisfactory if the change in reflection factor is measured. For measuring solar ultraviolet radiation, he finds the acetone-methylene blue the least applicable and the oxalic acid-uranyl sulfate reaction the most useful of these three methods. He presents a comparison of the data obtained by other workers with these methods, recalculated to absolute units.

Eisenschimmel [60] suggested the diminution of the active chlorine content of chloramine-T in 0.2*N* solution in methanol as a measure of the intensity of actinic light. The reaction was carried out in glass test tubes. No information as to the effective wave-lengths is available.

Weyde and Frankenburger [61] measure the erythema-producing region of the ultraviolet by the photochemical formation of crystal violet in an alcoholic solution of its leucocyanide or sulfite. For radiations of 3130A and 2537A, the quantum efficiency is one. A small quantity of potassium cyanide or sulfite is added to the alcohol solution. By using sufficiently thick layers of solution, it is possible to measure 10^{15} dye molecules, corresponding to 6.8×10^3 ergs. For ultra violet intensities of one erg per square centimeter, the exposure is one hour. Harris and Kaminsky [62] report that photolysis of crystal violet leucocyanide or sulfite is less desirable than photolysis of methylene-green leucocyanide for which the Einstein equivalence law (Chapter 12) holds with an accuracy of 2.5 per cent in absolute value and an average precision of 1.4 per cent for three wave-lengths. The latter reaction is said to be especially adapted for the measurement of very small light energies.

Anderson and Bird [63] used a fluorescence photometer with different chemical substances to measure the relative intensities of monochromatic ultraviolet light throughout the spectrum, and found that they could check the intensities as given by a thermopile. It was concluded that the photometric method may be employed for measuring accurately the ultraviolet energy.[64] Although fluorometers are simple and inexpensive,[65] Forbes [66] does not regard them as very precise.

Athanasiu [67] investigated the effects of light on voltaic cells. The latter were described as electrochemical actinometers. The maximum sensitivity of actinometers having electrodes of mercury salts in contact with 10 per cent sulfuric acid is at 2536A for mercurous chloride and at 2967 for mercurous bromide. The chloride and bromide are sensitive only to the ultraviolet; they are fluorescent under the latter, emitting a strong visible radiation. The effects were too great to be photoelectric and were attributed to photochemical changes at the surfaces of electrode-producing films. There are, in addition to an electrolyte, two similar metallic electrodes, one kept dark and the other irradiated. Polarization and thermal effects also play a part. With copper electrodes in copper sulfate, an

[59] Mayerson, H. S., *Am. J. Hyg.*, **22**, 106 (1935).
[60] Eisenschimmel, W., *Z. Zuckerind. Cechoslov. Rep.*, **51**, 535 (1927); *Chem. Abs.*, **22**, 356 (1928). The rate of combination of hydrogen and chlorine has been proposed as a measure of light intensity by C. Chilowsky, British P. 463,994, April 9, 1937, and 469,636, July 29, 1937; *Chem. Abs.*, **32**, 429 (1938).
[61] Weyde, E., and Frankenburger, W., *Trans. Faraday Soc.*, **27**, 561 (1932); U. S. P. 1,845,835, Feb. 16, 1932, of Frankenburger, W., Robl, R., and Zimmermann W.; *Naturwiss.*, **18**, 206 (1930); *Chem. Abs.*, **26**, 2121 (1932). Diazo compounds have also been employed in actinometers. N. V. Chemische Fabrik, L. van der Grinten, French P. 820,108, Nov. 4, 1937; *Chem. Abs.*, **32**, 5307 (1938).
[62] Harris, L., and Kaminsky, J., *J. Am. Chem. Soc.*, **57**, 1154 (1935).
[63] Anderson, W. T., Jr., and Bird, L. F., *Phys. Rev.*, **32**, 293 (1928).
[64] See also Croad, A. K., British P. 320,794 (1928).
[65] Winther, C., *Z. Elektrochem.*, **19**, 390 (1913); Gyemant, A., *J. Opt. Soc. Am.*, **12**, 65 (1926).
[66] Forbes, G. S., *J. Phys. Chem.*, **32**, 488 (1928).
[67] Athanasiu, G., *Compt. rend.*, **180**, 587 (1925); *J. Soc. Chem. Ind.*, 689A (1922); *Ann. Physique*, **4**, 318 (1925).

E.M.F. of the order of 40 millivolts can be obtained, the irradiated electrode being negative.[68]

Intensities of Various Lines as Related to Their Origins. The physical techniques described above have been applied to studies of the intensities of various lines and the results interpreted in terms of the probabilities of the occurrences of the corresponding transitions between energy states. These will not be discussed since the photochemist is more concerned with the broader features of the energy distribution of the spectral intensities within the various wave-lengths regions than with the physical theory of the intensities of individual lines.

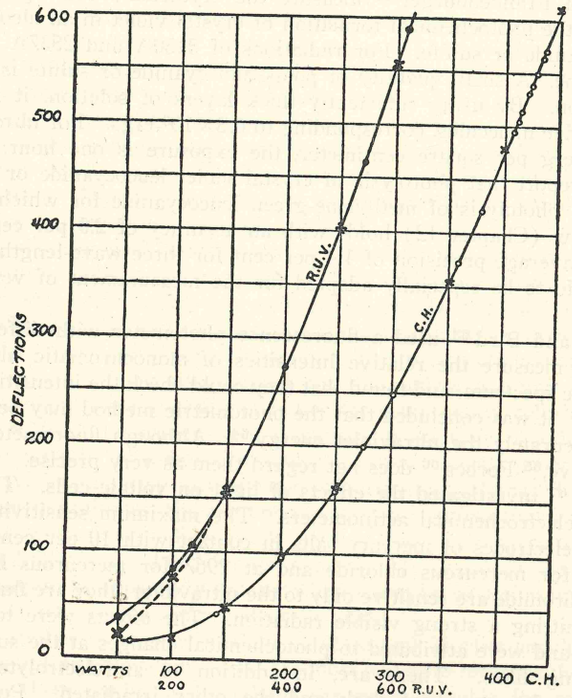


FIGURE 45. Variation in Total Radiation Emitted with Variation in Power Input (Coblentz, Long and Kahler, *Bureau of Standards Scientific Papers*).

DATA ON THE OUTPUT AND SPECTRAL DISTRIBUTION OF QUARTZ MERCURY ARCS

Hulburt [69] found the total radiation from 6000 to 2300A from a quartz mercury lamp as measured with a thermocouple to be 1.54×10^8 ergs per second. This would be equivalent to about 50 quanta emitted per mercury atom per second were all the energy at 5000A. Küch and Retschinsky [70] studied the spectral distribution

[68] See also Iimori, S., and Takebe, T., *Sci. Papers, Inst. Phys. Chem. Research, Tokyo,* **8,** 131 (1928).

[69] Hulburt, E. O., *Phys. Rev.,* **31,** 1109 (1928); **32,** 593 (1928).

[70] Küch, R., and Retschinsky, T., *Ann. Physik,* **20,** 563 (1906); **22,** 595 (1907); see also Pflüger, *Ibid.,* **26,** 789 (1908); Athanasiu, G., *Compt. rend.,* **178,** 2071 (1924); Shoda, M., *Japan. J. Physics,* **9,** 27 (1934); *Chem. Abs.,* **28,** 4310 (1934); Koch, B., *Ann. Physik,* **33,** 335 (1939).

of the energy from mercury arcs. They determined the total visible intensity and the intensities of individual visible lines by a flicker photometer, the ultraviolet by a photoelectric cell, and the continuous background by a photographic method. They also investigated absorption by mercury within the lamp.[71] Other early determinations of the energy distribution of this source were made by Ladenburg,[72] Hallwachs,[73] Fabry and Buisson,[74] Winther,[75] Allmand,[76] Souder,[77] Coblentz, Long and Kahler,[78] and Coblentz and Kahler.[79]

Coblentz, Long and Kahler give the variation of energy of wave-lengths less than 1.4μ as affected by variations in power input for a Cooper-Hewitt and an R.U.V. lamp. (Figure 45.) The experimental curves are closely represented by the formula $E = KW^x$, where for one lamp $K = 0.00462$ and $x = 1.83$ and for the other $K = 0.000457$ and $x = 2.314$.

Reeve [80] pointed out that the early work could not be used for a calculation of the absolute amount of energy emitted at any particular wave-length. He gave an intensity wave-length diagram for a 100-hour old Cooper-Hewitt 110-volt lamp operated at 62 volts and 4.2 amperes. In his diagram each "line" was given a triangular form, the base of the triangle being the wave-length region included. This method was adopted since the monochromator slit employed transmitted a finite range of wave-lengths rather than just the line width. Reflection and absorption losses, and the influence of compound lines, were considered.[81] For the relative energies of the mercury lines expressed in arbitrary units, he found the values given in Table 2.

Table 2.—Relative Energy of Mercury Lines.

Wave-length	Intensity	Wave-length	Intensity
248.5 mμ	7.1	303 mμ	82.5
254	39.5	313.5	213.0
265.5	35.1	334	9.4
270	6.6	366.5	326.0
275	2.3	406.5	111.4
280.5	20.3	437.5	166.6
290	17.9	559.	189.0
297	32.7	585.	207.

The early works contained some discrepancies in the ratios of the intensities of various lines. For example, Pflüger found that of the yellow line to the green line to be 140 to 90, while Ladenburg gave it as 27.4 to 42.9. The source of this and other discrepancies was attributed by Reeve to the influence upon the relative intensities of various lines of the electrical conditions, dimensions and age of the lamp.

A standard type commercial lamp run on 2.2 amperes and 10 volts per centimeter will deliver at an exit slit 40×1 mm. of a monochromator with 50 mm. objectives

[71] Küch, R., and Retschinsky, T., *Ann. Physik,* **22,** 852 (1907).

[72] Ladenburg, E., *Physik. Z.,* **5,** 525 (1904).

[73] Hallwachs, W., *Ann. Physik,* **30,** 593 (1909).

[74] Fabry, C., and Buisson, H., *Compt. rend.,* **153,** 93 (1911).

[75] Winther, C., *Z. Elektrochem.,* **20,** 109 (1914).

[76] Allmand, A. J., *J. Chem. Soc. Trans.,* **107,** 682 (1915).

[77] Souder, W. H., *Phys. Rev.,* **8,** 316 (1916).

[78] Coblentz, W. W., Long, M. B., and Kahler, H., *Bur. Standards Sci. Paper,* No. 330 (1918).

[79] Coblentz, W. W., and Kahler, H., *Ibid.* No. 378, 233 (1920).

[79] Coblentz, W. W., and Kahler, H., *Ibid.* No. 378, 233 (1920); see also Boll, M., *Compt. rend.,* **156,** 313 (1913); *J. Chem. Soc.,* **104,** 182 (1913).

[80] Reeve, L., *J. Phys. Chem.,* **29,** 39 (1925).

[81] Franklin, R., Maddison, R., and Reeve, L., *Ibid.,* **29,** 713 (1925).

and an aperture ratio 4.5, 8×10^3 ergs per second at 3660A and 4×10^2 ergs per second at 2800A, where the energy of a quantum is nearly a third greater.[82]

Beesley and Ridyard [83] recorded the energy distribution of a Uviol lamp burning at 29.5 volts and 2.42 amperes, and compared it with the data previously obtained by Allmand,[84] as well as with the energy distribution of the quartz mercury lamp. Their data are not included here as this lamp is now rarely used in photochemical work.

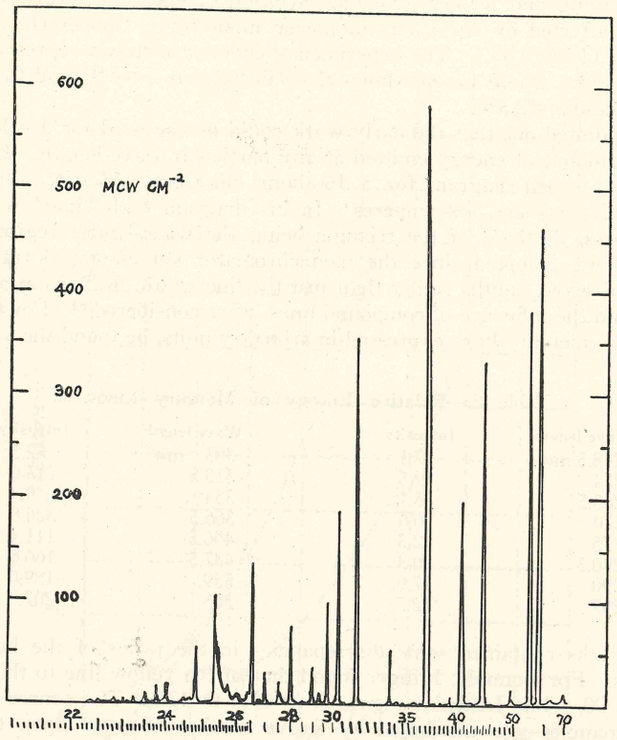


FIGURE 46. (McAlister, *Smithsonian Miscellaneous Collections.*)

Atkins and Poole [85] compared photochemical and photoelectric measurements of the radiation from a mercury vapor lamp. Andant and Lecompte [86] recorded the relative intensities of the principal lines from the yellow doublet to 2536A emitted by mercury vapor lamps of various designs functioning under different conditions. For the same arc, the intensity of emitted radiation changes greatly with the arrangement of the apparatus, especially with the voltage at the terminals. For two different arcs and for the same spectral line, an identical variation in each lamp does not produce the same effect on the emission.

[82] Forbes, G. S., and Harrison, G. R., *J. Am. Chem. Soc.*, **47**, 2449 (1925).
[83] Beesley, E., and Ridyard, H. N., *J. Phys. Chem.*, **32**, 1342 (1928).
[84] Allmand, A. J., *J. Chem. Soc.*, **107**, 682 (1915).
[85] Atkins, W. R. G., and Poole, H. H., *Sci. Proc. Roy. Dublin Soc.*, **19**, 355 (1929).
[86] Andant, A., and Lecompte, J., *J. Phys. Radium*, **1**, 65 (1930).

The relative intensities of prominent lines in the ultraviolet have been studied by Coblentz, Stair and Hague.[87] Absolute intensities in the visible and ultraviolet ranges have been recorded by McAlister.[88] In Figure 46 are given the intensities of 32 lines at 250 mm. from a 20 mm. midsection of a 400-hour-old Cooper-Hewitt direct current arc operated at high intensity (4.5 amperes and 150 volts). These values, expressed in microwatts per square centimeter may be multiplied by 7.1 to obtain approximate values for the full length of the arc exposed. Figure 47 gives similar data for the same arc operated at low intensity (3.0 amperes and 44 volts).

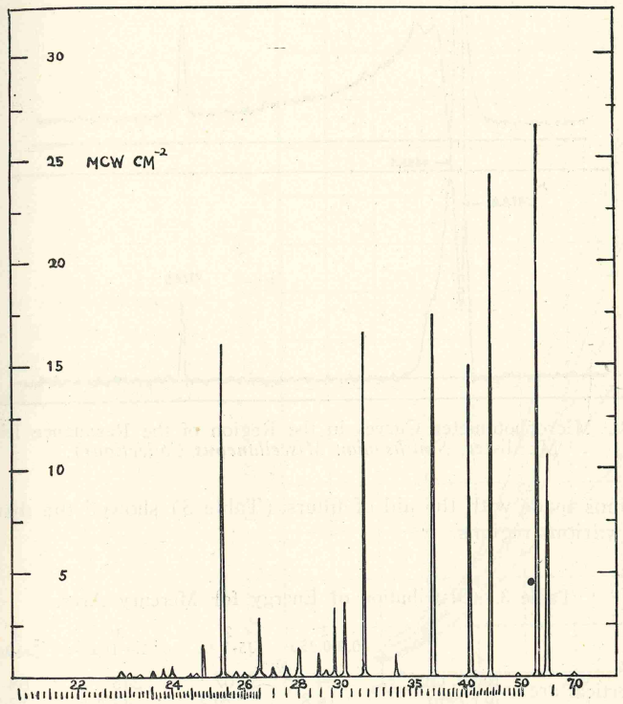


FIGURE 47. (McAlister, *Smithsonian Miscellaneous Collections.*)

In the former case the vapor pressure of the mercury is approximately atmospheric; in the latter it is but a few millimeters. Microphotometer curves of spectrograms in the region of the resonance line (Figure 48) show that even under low intensity conditions, the resonance line is partly reversed by absorption by mercury vapor, and that at high intensity conditions it is completely absorbed.[89] The mercury arc

[87] Coblentz, W. W., Stair, R., and Hague, J. M., *Bur. Standards J. Research*, **8**, 760 (1932).
[88] McAlister, E. D., *Smithsonian Miscellaneous Collections*, **87**, No. 17 (1933).
[89] Wood, R. W., [*Phil. Mag.*, **23**, 689 (1912)] found mercury vapor to absorb its resonance line so strongly that a quartz bulb filled with mercury vapor at room temperature (vapor pressure 0.001 mm.) casts a shadow when illuminated by this line alone. A thickness of 0.5 mm. reduces the intensity to one-third its initial value. This is not the only line absorbed by mercury vapor under arc conditions. Crew, W. H., and Dawson, L. H., [*J. Opt. Soc. Am.*, **17**, 261 (1928)] found some thirteen lines, including two "spark lines" to show self-reversal. For further studies, see Hughes, A., and Thomas, A., *Phys. Rev.*, **30**, 466 (1927); Mohler, F. L., and Moore, H. R., *J. Opt. Soc. Am.*, **15**, 74 (1927); Kopfermann, H., and Tietze, W., *Z. Physik*, **56**, 604 (1929).

usually employed apparently does not emit this resonance line. In the high intensity arc, the energy in this region is all due to the neighboring 2534.8A line and to the continuous background. Four different arcs showed differences averaging 5 per cent for some lines, the maximum being 10 per cent for the 2537A line.

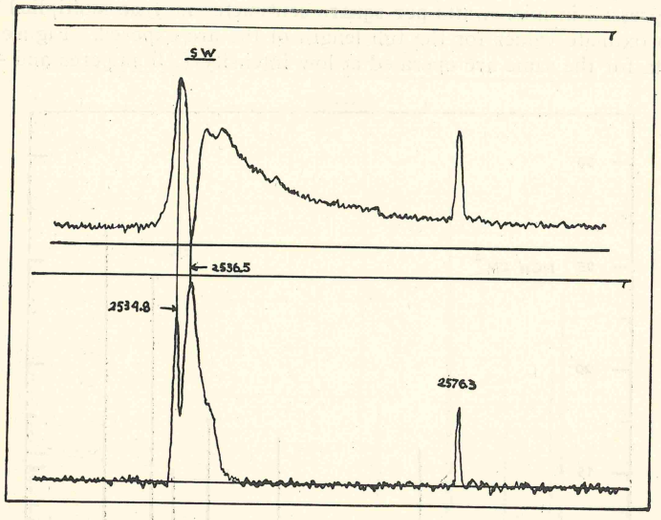


FIGURE 48. Microphotometer Curves in the Region of the Resonance Line (From McAlister, *Smithsonian Miscellaneous Collections*).

Observations made with the aid of filters (Table 3) showed the distribution of energy into various regions.

Table 3.—Distribution of Energy for Mercury Arcs.

		1 0.2-0.35μ	2 .35-1.4μ	3 1.4-19μ	4 >19μ	5 Total
High Intensity.						
20 mm. of vertical arc	mcw. cm.$^{-2}$	84	167	245	68	564
	per cent	14.8	29.7	43.4	12.1	100
Total vertical arc	mcw. cm.$^{-2}$	600	1130	2710	350	4700
	per cent	12.5	23.6	56.6	7.3	100
Total horizontal arc	mcw. cm.$^{-2}$	615	995	2700	370	4680
	per cent	13.2	21.2	57.7	7.9	100
Low Intensity.						
20 mm. of vertical arc	per cent	3.0	8.0	81.7	8.3	100
	mcw. cm.$^{-2}$	2.8	7.7	77.5	8.0	96
Total vertical arc	mcw. cm.$^{-2}$	19.8	59.6	704.8	124.	908.
	per cent	2.3	6.6	77.6	13.5	100.

Forsythe, Barnes and Easley [90] have compared the intensities, distribution, and output of ultraviolet radiation from the quartz mercury arc and several types of

[90] Forsythe, W. E., Barnes, B. T., and Easley, M. A., *J. Opt. Soc. Am.*, **21**, 30 (1931); **24**, 178 (1934).

"sun lamp" (see Chapter 8), and Waguet [91] has studied the light emission of mercury arcs at high pressure. Other relative data, obtained with a spectrometer and thermopile with galvanometer, were given by Oguri.[92]

It has been shown [93] that the spectrum of the light from a given mercury arc varies in character and intensity with the part of the lamp from which the light is emitted. The variation occurs because of irregularities in the thickness and curvature of the quartz envelope. For accurate spectrographic work, this source of error may be remedied by inserting a plane quartz window in the side of the burner.

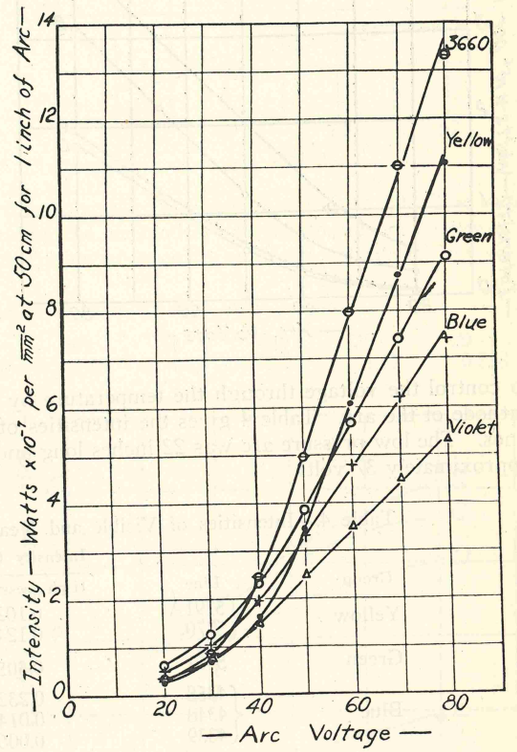


FIGURE 49.

Effect of Arc Voltage on Intensities of Line Groups (Johnson and Burns, *Journal Optical Society of America*).

Absolute line intensity and energy distribution data in high and low-pressure arcs were obtained by Johnson and Burns,[94] employing a method of photographic photometry (using as comparison a standardized mercury arc) developed by Stockbarger and Johnson. In this method, characteristic curves for the plates were taken for each line measured. Variations of the line intensity with current or voltage were measured on a quartz radiometer, and converted into absolute units by com-

[91] Waguet, P., *Compt. rend.*, **201**, 450 (1935). See also Kern, J., *Z. tech. Physic*, **19**, 249 (1938); *Chem. Abs.*, **32**, 8929 (1938), and Larché, K., and Rössler, F., *Physik. Z.*, **37**, 800 (1936); *Chem. Abs.*, **31**, 6549 (1937).

[92] Oguri, S., *J. Chem. Ind. (Japan)*, **38**, Suppl. binding, 392 (1935); **39**, 35, 143 (1936); *Brit. Chem. Abs.*, **B**, 635 (1936).

[93] Takahashi, T., and Clark, L. H., *J. Sci. Instruments*, **6**, 273 (1929).

[94] Johnson, L. B., and Burns, L., *J. Opt. Soc. Am.*, **23**, 55 (1933).

parison with the absolute values determined by photographic photometry at one current and voltage.

The vertical type high-pressure arc had an arc length of three inches. The current was kept at 4 amperes by a hand-controlled rheostat and the voltage was maintained at 45 volts by a voltmeter, photoelectric cell and an amplifier so arranged as

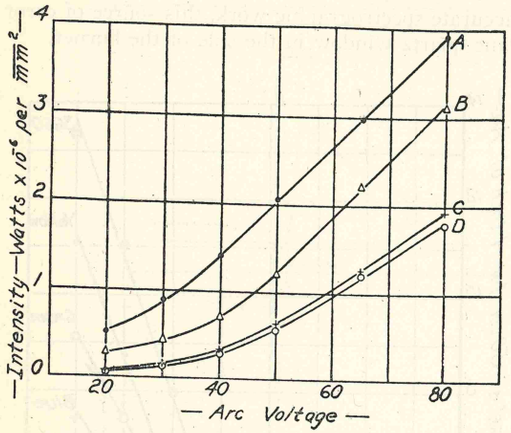


FIGURE 50.

Effect of Arc Voltage on Output in Four Spectral Regions (Johnson and Burns, *Journal Optical Society of America*).

to control the voltage through the temperature by regulating a blast of air on the cathode of the arc. Table 4 gives the intensities of the visible and near ultraviolet lines. The low pressure arc was 22 inches long and was operated at 4 amperes and approximately 37 volts.

Table 4.—Intensities of Visible and Near-Ultraviolet Lines.

Group	Line	Intensity (watts × 10⁻⁶/mm.² at 50 cm. for 1 inch of arc) High-pressure arc	Low-pressure arc
Yellow	5791A	0.102	0.009
	5770	0.124	0.010
Green	5461	0.305	0.057
Blue	4358	0.232	0.053
	4348	0.014	0.0008
	4339	0.006	0.0003
Violet	4078	0.022	0.0058
	4047	0.170	0.042
3660	3663	0.075	0.0068
	3655	0.086	0.0075
	3650	0.190	0.0126

Figure 49 shows the variation of the intensities of the line groups with arc voltage for the high-pressure arc carrying 4 amperes. The results confirm the data of earlier workers that lines of the same series (5461, 4358 and 4047, which give most of the radiation in their groups) increase in intensity together and retain their intensity ratios.

By the use of filters, the total radiation was divided into four regions (A, 14,000-40,000A; B, 3800-14,000A; C, 2950-3800A; D, 1850-2950A) and the variations of the intensities of each with arc voltage are shown in Figure 50. The total radiation for the whole arc, including the electrodes, was determined in microwatts per square mm. at 50 cm. The variation of intensity with the voltage is shown in Table 5.

FIGURE 51.

Effect of Arc Voltage on Relative Output in Various Regions (Johnson and Burns, *Journal Optical Society of America*).

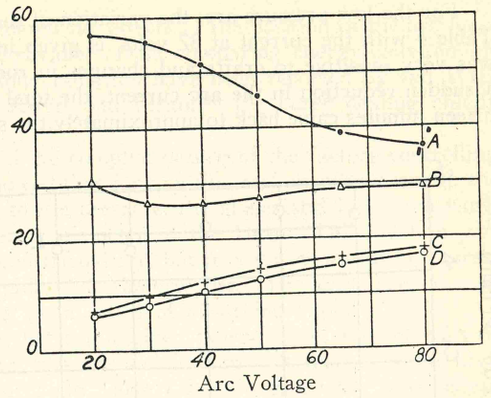
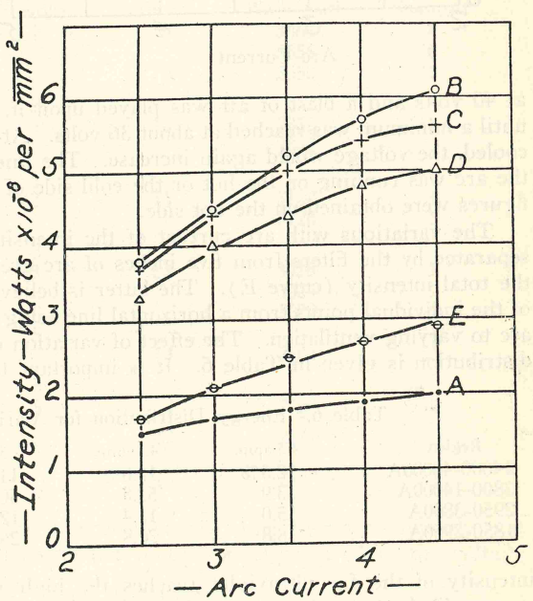


Table 5.—Variation of Intensity with Arc Voltage

Arc voltage	80	70	60	50	40	30	20
Intensity	10.74	8.60	6.50	4.43	2.72	1.57	0.888

FIGURE 52.

Effect of Current on Intensities of Line Groups (Low-pressure Arc) (Johnson and Burns, *Journal Optical Society of America*).



In Figure 51, the results secured are expressed in terms of the variation of the per cent of the total radiation in each of these regions with arc voltage (at 4 amperes).

For the low-pressure arc, the variation of the intensity of the groups of lines of Table 4 with the current at 37 volts, is given in Figure 52. The low-pressure arc was very sensitive to drafts and changes in room temperature. Immediately after a sudden reduction in the arc current, the total intensity went up, but after ten or fifteen minutes came back to approximately the same value. If the arc was running

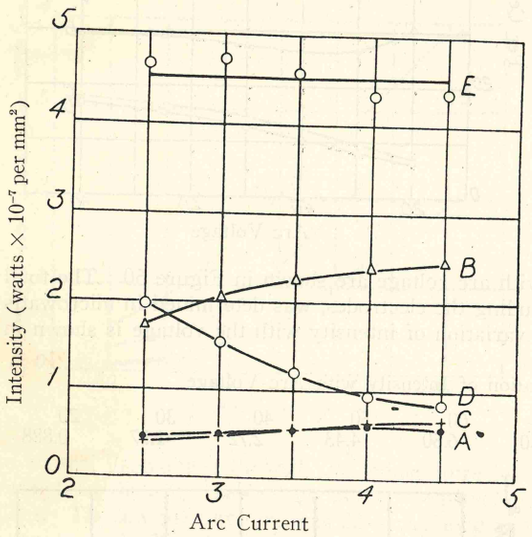


FIGURE 53.

Effect of Current on Output in Four Spectral Regions (Johnson and Burns, *Journal Optical Society of America*).

at 40 volts and a blast of air was played upon it, the arc voltage would decrease until a minimum was reached at about 36 volts. At this point, if the arc was further cooled, the voltage would again increase. The line intensity depended on whether the arc was running on the hot or the cold side of the minimum. The data in the figures were obtained on the hot side.

The variations with arc current of the intensities of each of the four regions separated by the filters from five inches of arc are given in Figure 53 along with the total intensity (curve E). The latter is believed to be constant, the variation of the individual points from a horizontal line being ascribed to the sensitivity of the arc to varying ventilation. The effect of variation of the arc current on the energy distribution is given in Table 6. It is important to note that at 2.5 amperes, the

Table 6.—Energy Distribution for Various Arc Currents.

Region	4.5 amp.	4.0 amp.	3.5 amp.	3.0 amp.	2.5 amp.
14000-40000A	12.3%	13.0%	11.9%	11.0%	9.9%
3800-14000A	53.9	52.8	50.0	45.0	37.8
2950-3800A	15.0	13.4	12.0	10.3	8.8
1850-2950A	18.8	20.8	26.1	33.7	43.5

intensity of the far ultraviolet reaches the high value of 43.5 per cent, and it appears likely that at lower currents, still higher percentages may be found, although the arc then becomes very unstable unless there is accurate temperature control of the surrounding air. Johnson and Burns also included data for the low-pressure arc in Uviol glass, and in UV 690 and UV 888 glasses.

Owen and Wright [95] have considered the effects of the position of the arc upon the spectroscopic analysis of the ultraviolet. Data comparing energy-emission for various artificial sources of ultraviolet radiation have been reported by van Wijk and Reerink,[96] Greider [97] and by Krefft and Pirani,[98] the latter dealing chiefly with sources of infrared rays.

Forbes and Leighton [99] indicated the complex nature of the factors controlling the intensity of a given line and showed that for any line and current strength, the maximum intensity is proportional to the pressure, the slopes and intercepts varying with the wave-length and internal diameter of the lamp. This relation was true up to five atmospheres in the constricted arc, but in a 9-mm. arc at high pressures the intensity increases less rapidly than the pressure. The latter phenomenon was attributed to the presence of a 3-mm. shell of absorbing vapor.

Harrison and Forbes [100] found that for a given power input, the intensity is much greater for high voltages and pressure and low current than it is for high current and low voltage and pressure. In Table 7 are given for the wave-length regions arbitrarily numbered in column 1 (including the lines in column 2) a rough estimate of the relative intensities of the various components of each group. The measurements were obtained with a spectroradiometer with a silver-bismuth thermopile. No corrections were made for reflection or absorption in the optical train, or for the effective slit-width. Only the relative intensities of single lines were measured.

Table 7.—Relative Intensity of Various Wave-lengths.

Group	Wave-lengths	Relative Intensity	Group	Wave-length	Relative Intensity
1, 2	selective quartz radiation	?	9	3663	4
				3655	6
				3650	10
3	11288A	2			
	10140	5	10	3352	..
				3342	..
4.	6234	1			
	6152	2	11	3132	4
				3126	5
5	5819	3			
	5804	3	12	3026	1
	5790	3		3024	2
	5769	6		3022	2
	5461	5			
			13	2804	1
7	4539	5			
	4348	5	14	2700	2
8	4078	3	15	2537	2
	4047	3			
			16	2438, etc.	1

Also, it was pointed out that the intensity of any line increases linearly (at constant current maintained by varying the ventilation of the arc) as the voltage

[95] Owen, E. A., and Wright, P., *Brit. J. Radiol.*, **5**, 330 (1932).
[96] van Wijk, A., and Reerink, E. H., *Physica*, **13**, 289 (1933).
[97] Greider, C. E., *Ind. Eng. Chem.*, **23**, 508 (1931).
[98] Krefft, H., and Pirani, M., *Z. tech. Physik*, **14**, 393 (1933).
[99] Forbes, G. S., and Leighton, P. A., *J. Opt. Soc. Am.*, **12**, 53 (1926)
[100] Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, **10**, 1 (1925).

gradient is increased beyond a limiting value which varies with the individual line and the current. Table 8 shows for the numbered groups the ratio of the intensities to that of the yellow-green lines (maximum or group five) for various voltages at 2.5 amperes. The energy of the 3660 line was found to be increased 17.1 times by

Table 8.—Relative Intensity of Groups to Yellow-Green Line.

	Ratio to Maximum Five (Yellow-green Lines) at				
Maximum	5 Volts	7 Volts	9 Volts	11 Volts	14 Volts
3	0.347	0.337	0.359	0.375	0.402
5	1.000	....	....	....	....
7	0.725	0.738	0.655	0.600	0.562
8	0.375	0.474	0.407	0.369	0.345
9	0.909	1.100	1.120	1.080	1.050
10	0.587	0.705	0.638	0.545	0.545
12	0.173	0.279	0.303	0.332	0.329
14	0.013	0.147	0.168	0.166	0.165
15	0.013	0.170	0.180	0.171	0.165

a 3.5-fold increase of the voltage gradient (from 4 to 14 volts per centimeter). Also it was stated that at 4.5 amperes and 25 watts per centimeter, only half as much energy will go into the yellow-green maximum as will when the current is 1.5 amperes and the voltage three times as great. For high efficiency, the arc should be cooled as little as possible. The ratio of intensities of any two lines of the same series was essentially constant.

The average arc shows the smallest change in energy distribution for a given variation in total intensity when the pressure is as high as possible. As this is the condition of greatest intensity of all the maxima, the best operating conditions seem to comprise as high a pressure and voltage drop as is consistent with the life of the lamp and with its mechanical structure.

Asada [101] proposes for the relation between the light intensity, the current and the potential difference, the expression, $G = kI(V-a)^n$, where G is the light intensity, k a constant, I the current, V the potential, a is a lamp constant determined as the least terminal voltage, and n is a constant for any given wave-length. The relation holds for both alternating-current and direct-current lamps, effective values being used in the former case. The value of n depends upon the type of current used.

Harris [102] found that there is a great outburst of ultraviolet energy from a cold lamp immediately after striking the arc, the current then having a maximal value and the resistance and voltage minimal values. This initial flare is quite evanescent, being followed by a sudden fall to the real onset of the permanent vaporizing and incandescent period. The latter begins after the first minute of arc striking has elapsed.[103] During the next two minutes, the voltage doubles and the lamp warms up, raising the vapor to incandescence. In the second and third minutes, a precipitous rise in emission occurs, the slope of which can be affected by controlling the temperature of the lamp. A blast of air causes the emission to rise slowly to its final value. A parabolic reflector behind the lamp reduces the rate of cooling on one side, so that incandescence is reached more quickly, but the emission falls again to a level slightly below that of the lamp under normal conditions in still air. For a constant source, the arc with a fan directed upon it, is to be chosen. Under these

[101] Asada, T., *J. Elec. Eng. Inst. (Japan)*, **51**, 36 (1931); *Chem. Abs.*, **26**, 1522 (1932).
[102] Harris, D. T., *Rev. Sci. Instruments*, **6**, 2 (1929).
[103] See also Watters, B. D., *Brit. J. Radiology*, **81**, 163 (1924).

conditions, devitrification and discoloration of the quartz is reduced, avoiding the rapid fall in efficiency most marked in the extreme ultraviolet. Figure 54 [104] shows in the left half the changes (on starting the Uviarc) which occur in the total energy, energy of the arc and electrodes, and arc alone, the latter only being concerned with the emission of the mercury lines. The right half of the figure shows in heavy lines the effect of cooling the arc on the increase of current, the energy expended in the arc, electrodes and arc and the total watts. In lighter lines are shown the corresponding effect of increasing the series resistance. Maddock [105]

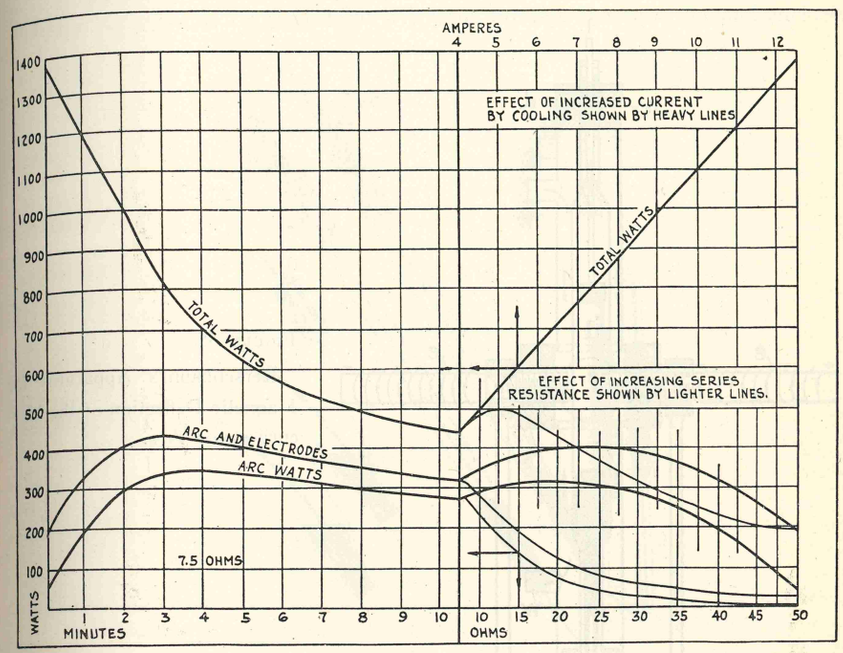


FIGURE 54. Energy Distribution under Various Operating Conditions (Buttolph, *Review Scientific Instruments*).

plotted arc watts—intensity variation curves for temperature variation of the air surrounding the burner, and tabulated absolute intensities for thirty lines between 7000 and 2300A.

MEANS FOR INCREASING THE OUTPUT OF THE RESONANCE LINE

To issue from the lamp the light of the bright radiant axial thread must first penetrate the envelope of vapor and undergo absorption. To obviate this absorption effect the temperature of the envelope may be reduced thereby lowering the vapor pressure. This can be effected by cooling with water, but owing to condensation of mercury vapor, a coating of mercury may form on the inside wall of the lamp and prevent the issuance of light. Another method of preventing the limita-

[104] Buttolph, L. J., *Rev. Sci. Instruments*, **1**, 497 (1930).
[105] Maddock, A. J., *Proc. Phys. Soc. (London)*, **47**, 424 (1935).

tion of the output by absorption, used particularly in lamps for the study of resonance phenomena where a strong emission of the resonance line is required, is based upon [106] deflection of the arc toward one side of the tube of the lamp by means of an electromagnet. This operation is said to raise the temperature of the tube at the place where the arc is applied, thus burning an aperture in the film resulting from condensation. The light of the deflected radiating arc will issue through this aperture without having penetrated an absorbing layer of mercury vapor. Figure 55 shows the construction of this apparatus.

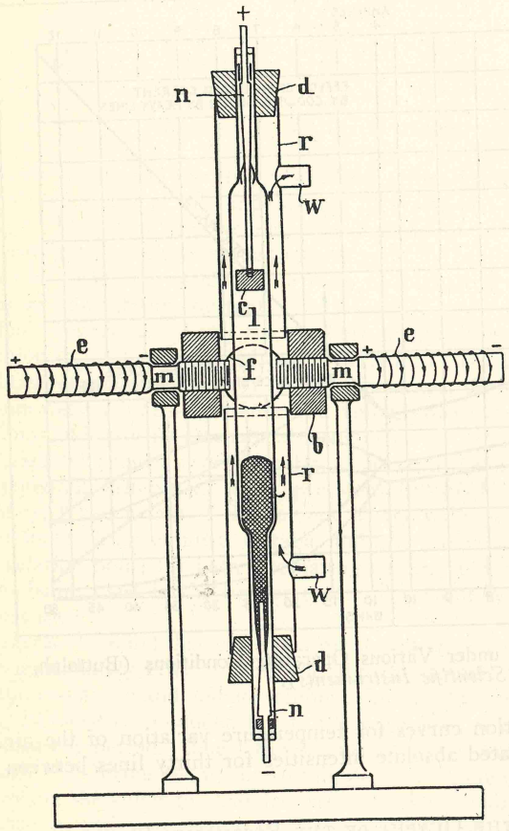


FIGURE 55.

Kerschbaum's Apparatus for Magnetic Deflection of the Mercury-vapor Arc.

The brass block (b) has a vertical bore; into this are soldered two tubes (r) having branches (w) for receiving and discharging the cooling water. Into this vertical cooler is inserted a quartz mercury-vapor lamp (1), which is fastened above and below by means of bored rubber stoppers (d). The quartz lamp is a vertically burning lamp, which is of the simplest and most compact construction possible. As leading-in members for the lamp, ground-in nickel-steel pins (n) serve. Only the metal of the lower electrode (cathode) is mercury. The anode

[106] Kerschbaum, F., U. S. P. 1,118,868, November 24, 1914; *Chem. Abs.*, **8**, 2315 (1914).

is a piece of carbon (c) screwed on the end of the upper nickel-steel pin. The brass block (b) has in addition two lateral, horizontal, threaded bores. By means of these apertures the ends of two iron rods (m) are screwed up close to the wall of the lamp; over these rods are pushed coils of wire (e). Each of the two coils has 200 turns of covered copper wire of ½ ohm resistance; the current employed is 2 to 3 amperes. The electromagnets so formed produce lines of force at right angles to the axis of the lamp. The block (b) has another horizontal bore (f). This passes through only the rear half of the block and can be closed by a quartz plate. When the lamp is burning and the electromagnets are so connected that they deflect the arc to the rear, the light will issue through the bore (f) and enclosing

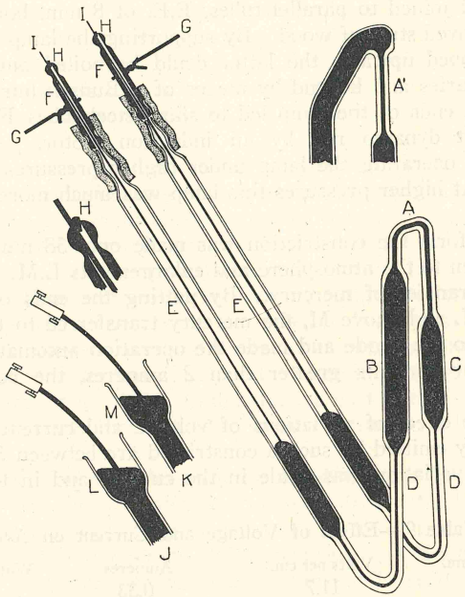


FIGURE 56. Diagram of the constricted arc, arranged for pressures up to five atmospheres and currents from 0.2 to 2.0 amperes. The inserts show at A' the modified form of the constricted portion, arranged to water-cool the hot column so that currents up to 5.0 amperes could be used, and below the enlarged ends arranged for work at atmospheric pressure (Forbes and Harrison, *Journal of the Optical Society of America*).

quartz plate. The arc is drawn by rotating the lamp into its horizontal position. Tanberg [107] has studied the physical phenomena involved in the passage of a mercury arc at low vapor pressure in a magnetic field.

The Constricted Arc. In these arcs the non-luminous portion of the arc is eliminated by making the tube of such narrow diameter that it is practically completely filled by the narrow luminous thread. They are usually laboratory made, and may be operated at pressures up to about 5 atmospheres, but are comparatively short-lived. Harrington [108] described a lamp operated on 25 volts

[107] Tanberg, R., *Nature*, **124**, 371 (1929). See also Fabrikant, V. A., and Rokhlin, G., *Compt. rend. acad. sci. U.R.S.S.*, **19**, 393 (1938); *Chem. Abs.*, **32**, 8256 (1938).

[108] Harrington, E. L., *J. Opt. Soc. Am.*, **7**, 689 (1923).

direct current (10 volts per centimeter), yielding a brilliant light of capillary tube dimensions.[109] Vincent and Biggs[110] described an arc with a 0.3 mm. column, open to the air and carrying 0.1 to 0.16 ampere at 100-150 volts; it had low current capacity. Harrison and Forbes[111] designed two special lamps. The first of these (Figure 56) had in A a bent tube 63 mm. long, of 2.0 mm. bore and 7 mm. external diameter. It extended between two mercury reservoirs, one at a higher level than the other. The one at the higher level was made negative, so that it would not fall as the result of the transfer of mercury by the current. The tubes (B and C) of 5 mm. internal diameter joined the ends of the arc tube to capillaries DD of 0.5 mm. bore and 11 cm. long. Their purpose was to restrain oscillations but they were large enough to carry 5 amperes without undue heating. These were bent through 135°, and joined to parallel tubes, E,E, of 8 mm. bore and 20 cm. long, mounted on a grooved strip of wood. By supporting the lamp so that BAC sloped down and EF sloped upward, the latter could be boiled out in a few minutes through the capillaries and beyond by means of a Bunsen burner, no pump being needed. The open ends of the lamp led to short steel tubes FF soldered to leads GG of a 550-volt dynamo run by an induction motor. Arrangements were described also for operating the lamp under higher pressures obtained by means of a tire pump. At higher pressures this lamp was much more effective than arcs of greater section.

In a modified form the constriction was made only 38 mm. long, the ends of the tubes were open to the atmosphere and enlargements L,M, retarded changes in level due to the transfer of mercury. By putting the ends of a long U trough under the end of L and above M, the mercury transferred to the cathode trickled down the trough to the anode and made the operation automatic. Three amperes were required; for currents greater than 2 amperes, the constriction must be water-cooled.

In Table 9 the effect of variations of voltage and current upon the pressure in and the intensity emitted by such a constricted arc between 3650 and 3663A are listed. A 15-fold variation was made in the current and in the voltage, but not

Table 9.—Effect of Voltage and Current on Arcs.

Pressure, mm.	Volts per cm.	Amperes	Watts per mm.^{2} × 10^{-6}
88	11.7	0.33	7.00
654	28.4	0.33	39.0
3920	57.6	0.33	268.
29	7.4	1.00	15.0
208	13.8	1.00	43.0
664	21.4	1.00	137.
1398	28.2	1.00	392.
752	21.7	3.02	940
752	27.8	4.00	2090
752	29.5	5.00	2600

in these simultaneously; the result was a 160-fold variation in pressure and a 400-fold variation in the intensity of the 3660 line. The authors gave graphically the intensity vs. voltage-gradient curves at one ampere for six different wave-length maxima, as well as at 0.33 ampere (12-58 volts per cm.) for pressures ranging from 0.1 to 5 atmospheres. The first arc constructed had a section of 50 square

[109] Harrington, E. L. See also *Phil. Mag.*, (7) **4**, 836 (1927).
[110] Vincent, J. H., and Biggs, G. D., *J. Sci. Instruments*, **1**, 242 (1924).
[111] Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, **11**, 99 (1925); *J. Am. Chem. Soc.*, **47**, 2449 (1925).

mm., a later one of about 3. The curves for the first showed a sharper bend and a straighter upper portion; those of the constricted arc showed a more uniform curvature. The curves for the larger arc bent and began to ascend steeply at about 6 volts per cm., but in those of the constricted arc this occurred at about 20 volts per cm. There was no evidence of a decrease in efficiency as the pressure increased up to five atmospheres.

The absorption of all lines, especially of 2537A, the shortest mercury arc line of sufficient intensity for general use in photochemical work, was diminished in the constricted arc. This line could be kept at constant intensity by tripling the current from 0.33 to 1.00 ampere, and cutting the voltage down from 62 to 32 volts per cm., thereby reducing the pressure from 4000 to 1500 mm. The greatest advantage of this type of arc seemed to lie in its high internal resistance, giving higher efficiencies at normal pressures, so that an increase in current becomes more nearly equivalent to an increase in voltage in the production of higher intensities. There was a tremendous relative increase in the 3663A line at high currents, while all the ultraviolet maxima except that at 2537A showed higher relative values at high currents.

For studying reactions with very low photochemical yields, there is required a source giving very great light intensities with at the same time a high degree of spectral resolution. These requirements were most nearly met by a portable constricted arc between two mercury surfaces, confined in a water-cooled quartz tube of 2 mm. internal, and 7-mm. external, diameter, 38 mm. long, with its ends open to the atmosphere. This lamp could be repaired easily and could be refilled and boiled out in ten minutes. There were no sealed-in leads to fail, no possibility of damage on reversing the polarity, and no tungsten electrode to sputter, the latter being a chief cause of the decrease in ultraviolet output of other arcs.[112] The constricted arc furnished (per square millimeter of exit slit of a monochromator) energy flux up to 30 times that available from a commercial lamp run at normal rating.

A further modification was designed by Leighton and Forbes[113] to combine as fully as possible the long life of large diameter arcs with the high intensity of the constricted arc. The legs of an inverted U of 6 mm. internal diameter dipped into mercury reservoirs left open to the atmosphere. A 5-mm. capillary, nearly filled with an iron wire, attached to each arm of the U rendered oscillation negligible. The electrodes were water-cooled, and by adjusting the relative heights of the water and electrode surfaces, mercury transfer was neutralized. The distribution of the energy flux (determined by the aid of a monochromator and thermopile) is given in Table 10.

Table 10.—Distribution of Energy Flux.

A	10,140	5770	4350	4060	3660	3130	3020	2800
Ergs/sec. mm.^{2}	325	910	490	360	900	610	420	100
A	2700	2540						
Ergs/sec. mm.^{2}	150	99						

Crist[114] gave directions for making an arc that will run at 4 to 4.5 amperes and 20-25 volts per centimeter for over thirty hours with fairly constant intensity.

[112] Fabry, C., and Buisson, H., *Compt. rend.*, **153**, 93 (1911).
[113] Leighton, P. A., and Forbes, G. S., *J. Am. Chem. Soc.*, **51**, 3550 (1929).
[114] Crist, R. H., *J. Am. Chem. Soc.*, **52**, 4337 (1930).

He later [115] put a transverse magnetic field across the arc to displace the latter to the back wall, thereby decreasing devitrification at the front wall. Other capillary mercury-vapor lamps have been described by Heidt and Daniels,[116] by Heidt and Forbes,[117] and by Hoffman and Daniels.[118] The model of Forbes and Heidt eliminated cemented joints and the objectionable capillaries used in the earlier lamps to check mercury oscillations. Quartz tubing of 8-mm. internal diameter was used. Figure 57 is an axonometric view of the device, which was about 30 cm. in height. One feature of the apparatus is the tapered "Pyrex" plungers P, ground into tapers in the quartz walls at J. After the lamp is filled, these plungers are lowered

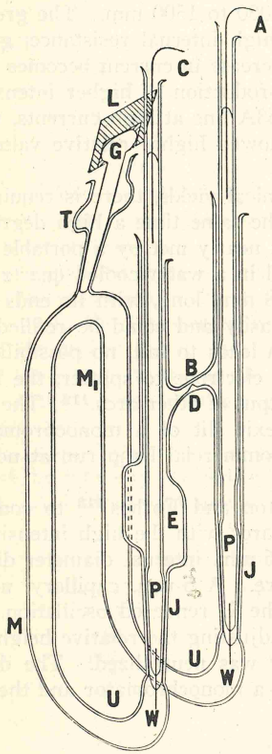


FIGURE 57.

Quartz Mercury-vapor Lamp of Forbes and Heidt (*Journal American Chemical Society*).

until oscillations of mercury are negligible, but the plungers are not lowered quite enough to close the joints completely; otherwise the lamp will melt or blow up. Tungsten wires W are sealed into the ends of the plungers, and when the latter are filled with mercury, a current path of negligible resistance, incapable of arcing, is provided. The two tubes U stand in open rectangular copper tanks (not shown), about 160 mm. (right) and 60 mm. (left) deep. Obviously, the length of either side of the arc (in one case, 150 mm. from M to M_1) can be changed by varying

[115] Crist, R. H., *J. Am. Chem. Soc.*, **54**, 3939 (1932).
[116] Heidt, L. J., and Daniels, F., *J. Am. Chem. Soc.*, **52**, 2151 (1930); **54**, 2381 (1932).
[117] Heidt, L. J., and Forbes, G. S., *J. Am. Chem. Soc.*, **53**, 4349 (1931).
[118] Hoffman, R. M., and Daniels, F., *J. Am. Chem. Soc.*, **54**, 4226 (1932).

the depth of the corresponding tank. Tubes soldered in, top and bottom, permit rapid circulation of water.

The lamp is filled and boiled out through the tap T, provided with a ground-in quartz plug G held down by the lead weight L and sealed with mercury. The tap is bent 30° from the vertical, to prevent hot air ascending during operation from distilling the mercury out of the lamp. After closing the circuit through a suitable resistance, the arc is started by holding a flame below T. This arc sinks to the water surfaces, and operates at 3.5 amperes and 170 volts. As a much larger amount of mercury is displaced on the cathode side, the enlargement at E is necessary to accommodate it. As the mercury distils from the hot cathode to the cooler anode, it returns by the bridge B, which has a dam D to break up the trickles into

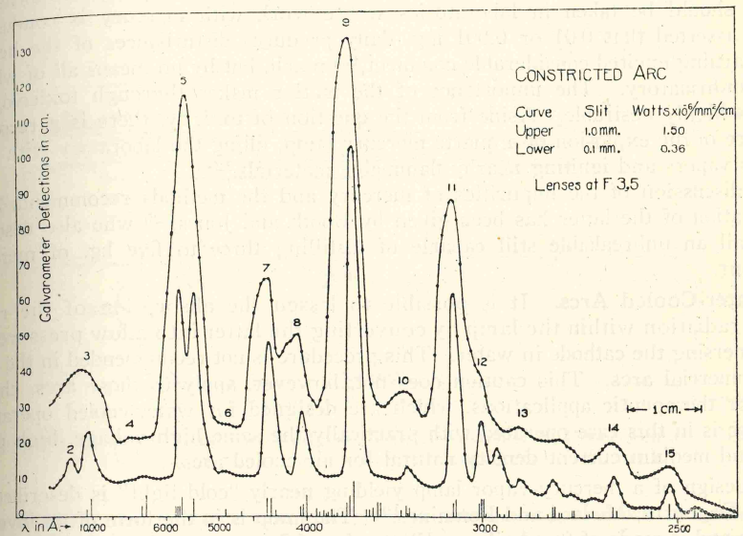


FIGURE 58. Spectral Energy Distribution Curves for the Constricted Arc (Forbes and Harrison, *Journal American Chemical Society*).

drops and thus avoids momentary short circuits. With a steady source of current, and nearly constant barometric pressure and ventilation, the total variation in light intensity over considerable periods seldom exceeds 3 per cent.[119]

Forbes and Harrison [120] presented a wave-length vs. energy curve (Figure 58) for a constricted arc in a water-cooled quartz tube of 2 mm. internal and 7 mm. external diameter, 38 mm. long with its ends open to the air and running on 3 amperes and 90 volts. A monochromator was used as a spectroradiometer. The lower curve, showing greater resolution, was obtained with an entrance slit of 0.1 mm., and the upper one with 1 mm. In the latter case, 140 ohms resistance was in series with the galvanometer and thermopile so that 1.0 cm. deflection corresponded to 1.50 microwatts per square millimeter at the exit slit. In the lower curve, 0.36 microwatt was the corresponding figure. Along the wave-length axis are short,

[119] For a simple magnetic method of starting this lamp, see Wilson, L. D., *J. Am. Chem. Soc.*, **58**, 856 (1936).
[120] Forbes, G. S., and Harrison, G. R., *J. Am. Chem. Soc.*, **47**, 2449 (1925).

vertical lines indicating the number and approximate relative intensities (in a given group) of the various lines making up each maximum, as determined from a spectrogram of the light from the arc taken with an instrument of higher resolving power; the weaker lines are all relatively fainter than indicated. At the highest intensities used with the constricted arc, 490 microwatts per square millimeter of approximately monochromatic light of 3660A were issuing from a monochromator slit 1 × 40 mm. or a total energy flux of about 196,000 ergs per second. Elenbaas [121] has described a water-cooled constricted arc which operates under mercury pressures of 5 to 25 atmospheres.

In working with laboratory-made lamps, caution must be taken to avoid mercury poisoning. Attention was directed to the insidious onset of mercury poisoning and to the difficulty of cure by Stock,[122] who described details of hygienic measures which should be taken in laboratories where work with mercury is conducted. Stock asserted that 0.01 or 0.001 mg. daily produces disturbances of the health. His warning excited considerable comment,[123] much, but by no means all of which, was confirmatory. The importance of the matter makes thorough toxicological studies highly desirable. Aside from the question of toxicity, there is a recorded instance of the explosion of a quartz mercury lamp, filling the laboratory with dangerous vapors and igniting nearby flammable materials.[124]

A discussion of the impurities of mercury and the methods recommended for purification of the latter has been given by Booth and Jones,[125] who also describe in detail an unbreakable still capable of distilling three to five kg. of mercury per hour.

Water-Cooled Arcs. It is possible to lessen the absorption of the resonance radiation within the lamp by converting the latter into a low pressure arc by immersing the cathode in water. This procedure is not recommended in the case of commercial arcs. This caution does not, however, apply to those arcs, chiefly sold for therapeutic applications, which are designed for water-cooled operation. The arc is in this case operated with practically the same high voltage, high pressure and medium current density natural for air-cooled arcs.

A design of a mercury-vapor lamp yielding nearly "cold light" is described by Billon-Daguerre, Medard and Fontaine.[126] The lamp is in the form of an inverted U-tube and is made of fused silica. Electrodes of Invar enter the ends of the tube. A short intense arc is formed at the bend of the tube between the columns of mercury on either side. The lamp is enclosed in a transparent silica flask (the wall of which is paraboloidal and silvered to act as a reflector) and is immersed in a tank of water. The light is concentrated by the mirror and emerges through a silica window in the tank. The lamp consumes 18 amperes, either alternating or direct current at 70 volts, and yields 3000 candlepower. The light can be used for microscopy and projection work without heating the specimens or celluloid films. The mercury lamp is said to possess an advantage over the carbon arc in that the

[121] Elenbaas, W., *Rev. optique*, **15**, 343 (1936). See also Harada, T., and Azuma, T., *Proc. Phys.-Math. Soc. Japan*, **19**, 677 (1937); *Chem. Abs.*, **31**, 8365 (1937); Egyesült Izzólampa és Villamossagi R. T., British P. 482,070, March 23, 1938; *Chem. Abs.*, **32**, 6562 (1938); Bol, C., *Phys. Rev.*, **52**, 214 (1937).

[122] Stock, A., *Z. angew. Chem.*, **39**, 461, 984 (1926); **41**, 663 (1928); *Biochem. Z.*, **216**, 243 (1929).

[123] Schmidy, A., *Z. angew. Chem.*, **39**, 786 (1926); Pincus, G., *Ibid.*, 787; Reihlan, H., *Ibid.*, 788; Wolf, L., *Ibid.*, 789; Ruska, J., *Ibid.*, 790 (1926); Hoffmann, F. G., *Chem. Ztg.*, **50**, 927 (1926); Holtzmann, *Z. angew. Chem.*, **40**, 438 (1927); Winderlich, R., *Chem. Ztg.*, **52**, 629 (1928); Kröner, W., *Chem. Ztg.*, **52**, 121 (1928); Podrouzek, R. N. V., *Chem. Listy*, **22**, 529 (1929).

[124] Mechlin, F. J., *Ind. Eng. Chem.*, **19**, 859 (1927).

[125] Booth, H. S., and Jones, N. C., *Ind. Eng. Chem.*, **19**, 104 (1927).

[126] Billon-Daguerre, A. L., Medard, L., and Fontaine, H., *Compt. rend.*, **157**, 921 (1914).

luminous point remains fixed and requires no regulation. Application of such lamps to water sterilization and submarine photography has been suggested.

Bates and Taylor [127] developed a cooled arc of C702P "Pyrex" glass with tungsten leads. Through the center were two concentric quartz tubes, R_1 and R_2 (Figure 59). R_1 is the reaction vessel for photochemical changes while R_2 is a water-jacket to prevent R_1 from becoming overheated by the action of the arcs. Outside, the glass system was sealed to quartz by rubber tape and by Gooch crucible tubing, wired and shellacked to permit operation of the arc at 100°C. The seals were protected by coils of lead pipe D carrying cold water. N is the negative electrode and A,B,C_1 and C_2 are all positive. N and A are tungsten leads covered by just enough mercury to cause the two surfaces to come together on jarring. An arc is formed which jumps to B, a nickel cone welded to tungsten.

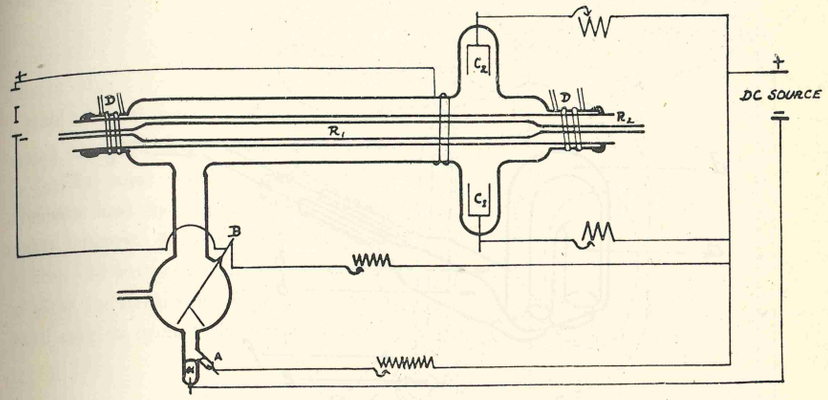


FIGURE 59. Mercury Arc for Study of Mercury-Sensitized Photochemical Reactions (Bates and Taylor, *Journal American Chemical Society*).

This serves as an electrode and also deflects mercury vapor from N against the walls of the bulb, kept in a water bath. This regulates the vapor pressure in the arc to that of mercury at the bath temperature. The arc can be brought up to the electrodes C_1 and C_2 by breaking down the space charge by an induction coil, the secondary of which is shown at I. C_1 and C_2 are two cylindrical nickel electrodes. The potential necessary depends to a large extent on the geometry of the arc. R_2 is 2.5 cm. in diameter and 45 cm. long, R_1 1.5 cm. by 37 cm., the surrounding glass arc being 40 cm. by 5 cm. The side tubes containing C_1 and C_2 are 3.5 cm. in diameter and 5 cm. long. The side tube with bulb and mercury reservoir is 30 cm. long and 3.5 cm. in diameter, while the diameter of the bulb is 6 cm. This has a drop of 35 volts from C_1 and C_2 to N when running at 18 amperes. The slide-wire resistances are of such size and capacity that the current from A to N is 0.5 ampere, B to N, 5 amperes, and from C_1 to C_2 to N up to 10 amperes each. C_1 and C_2 must have separate resistances or the current would flow entirely to one of them, giving an unevenly distributed discharge. After the arc has been started, B may be disconnected, but A should remain in the circuit to insure a steady arc. Due to leaks around the seals, the arc can be run only with a mercury pump in con-

[127] Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **49**, 2438 (1927).

tinual operation. If the arc is run with air in too large quantity, not only do the electrodes become oxidized, causing the arc to emit a pink glow, but the mercury tends to wet the glass between A and N making it impossible to start the arc. When the arc is first set up or after a long period of disuse, the nickel electrodes must be degassed by the passage of a current greater than that ordinarily used. The temperature of the water in R_2 should be kept above that of the bulb to prevent distillation of mercury from N, which would cut down the light.

A water-cooled lamp of the mercury anode type is in extensive use for medical work. The cooling serves to protect the tissues from the heat of the arc, so that it is possible to secure a high intensity of ultraviolet, particularly in the short-wave region, by reducing the distance between the source and the area treated. The lamp has a U-shaped quartz tube, *A*, the bend of which is in a plane perpendicular to the plane of the arms. (Figure 60.) The tube carries on the ends two mercury containers *BB* at right angles to the plane of the arc tube, and these constitute the electrode vessels to which the current is conducted by ground-in mercury-sealed rods *CC*. The arc is formed in the portion of the tube which is surrounded by a jacket of quartz, so shaped as to maintain an approximately equal distance between the walls of the tube and the envelope, to make the cooling uniform. The space is filled with a suitable gas, the thermal conductivity of which affects the electrical characteristics of the arc.[128] Between this jacket and the outer housing of the apparatus, water is circulated. The light is emitted through a quartz window in front of the casing, after passing through a layer of water. The compact form made possible by this construction, known as the Kromayer,[129] is advantageous for many purposes. A form with a double anode for alternating current operation also has been prepared.

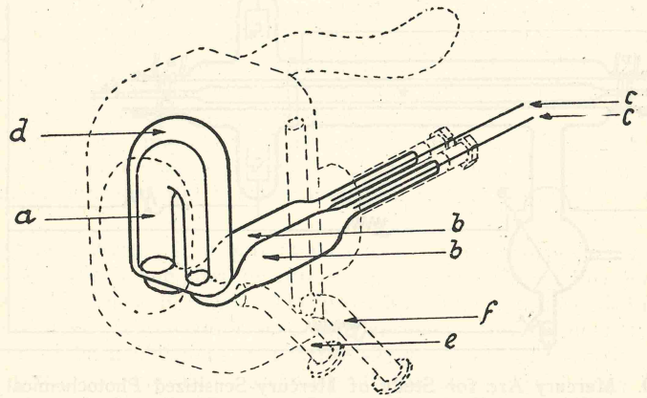


FIGURE 60. Kromayer Lamp.

Other manufacturers, notably the Burdick Corporation, employ the Uviarc as the source for a water-cooled lamp. The infrared rays are removed by a sealed quartz filter cell containing pure water. The cell is incompletely filled to permit

[128] Anderson, W. T., Jr., U. S. P. 1,749,994, March 11, 1930 (to Hanovia Co.); British P. 296,527, Sept. 6, 1928; French P. 638,802, Aug. 3, 1927; British P. 356,056, Sept. 3, 1931.

[129] Hanovia Chemical and Manufacturing Co.

expansion of the water as the lamp heats up. A stream of flowing water surrounds the filter cell and serves to cool it. This stream of water does not come into contact with any quartz surface through which the rays must pass, eliminating any loss of transparency due to the deposition of solids. An air-space between the filter-cell and the quartz face of the lamp further eliminates heat by conduction. See Figure 61. An automatic shutoff to protect the lamp when the water flow fails has been described by Piatti.[130] Another liquid-cooled lamp for photochemical work is due to Goltstein.[131]

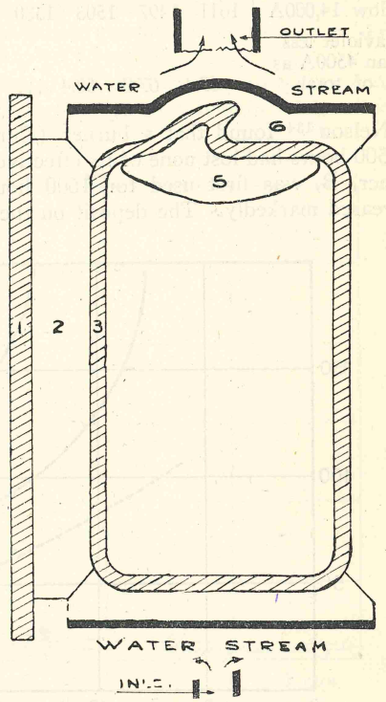


FIGURE 61.

Ever-Clear Window of Burdick Water-cooled Lamp. Cross Section: Side View. 1. Quartz outer face. 2. Air space to eliminate heat by conduction. 3. Fused quartz window. 4. Lens of distilled water to filter out infrared. 5. Evacuated space to allow for expansion of water. 6. Soft-metal case to protect the quartz window.

Courtesy Burdick Corporation.

THE DETERIORATION OF QUARTZ MERCURY ARCS

Deterioration of the lamps was a serious problem to the earlier manufacturers of mercury arcs. The literature is filled with many observations of lamp failure. Poorly constructed lamps caused some of these.[132] Others were inaccurate because of the use of unsatisfactory actinometric methods for measuring the output.

In early lamps, Coblentz found that the percentage of the total radiation shorter than 4500A decreases from an initial value of 70 per cent to about 50 per cent after 1000 to 5000 hours. This included the strong groups of lines at 4360 and 4060A.

[130] Piatti, L., *Physik. Z.*, **31**, 182 (1930).

[131] Goltstein, E., U. S. P. 1,669,819, May 15, 1928; *Chem. Abs.*, 22, 2296 (1928). For a recent inexpensive source of mercury resonance radiation of high intensity, see Steacie, E. W. R., and Phillips, N. W. F., *Can. J. Research*, **16B**, 220 (1938).

[132] See, *e.g.*, Bordier, H., *Arch. Elec. Med.*, **1910**, 396; Courmont, J., and Nogier, T., *Compt. rend.*, **152**, 1746 (1911); *Illuminating Engineer*, London, **4**, 503 (1911); Le Bon, G., *Compt. rend.*, **153**, 49 (1911); Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453 (1925).

The total output decreased to about one-half to one-third of its initial value.[133] Thermopile observations showed no marked difference in the proportion of ultraviolet emitted during the first 500 hours of use. The data of Table 11 represent the output as measured in galvanometer scale deflections.

Table 11.—Effect of Age upon Radiation.

Age in hours	0	97	177	343	450	522	640	783	959	1064	1140
Total radiation below 14,000A	1611	1497	1503	1380	1033	910	1104	1107	1069	1025	1034
Ultraviolet less than 4500A as % of total	69.4	67.8	60.4	...	59.9	58.2	54.8	52.3	50.8	...	49.1

Nelson [134] found that a burner (Curve A, Figure 62) which had been used for 500 hours had lost none of its effectiveness in testing ageing on paints. Another burner, B, was first used for 1600 hours, at which time its effectiveness had decreased markedly. The deposit on the surface of the quartz was then removed

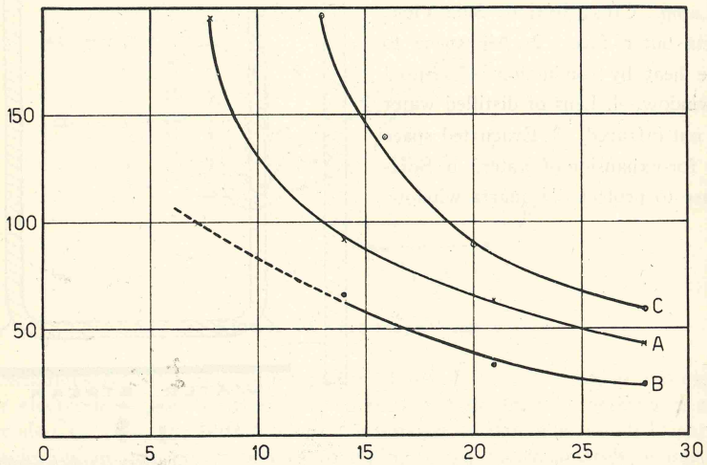


FIGURE 62. (Nelson, *Proceedings American Society for Testing Materials.*)

as far as possible by heating the quartz with a blast burner and the lamp again used for 250 hours. The relative intensities of the two burners A and B in the region shorter than 3100A were found to be in the ratio of 1.7 to 1 when used at 220-240 volts and 6.5 amperes, indicating a decrease of about 40 per cent for the old burner.

Reeve [135] found by physical methods that 500 hours of use caused a decline in the intensity of a commercial lamp at 2540A of 60 per cent and of the 3660A lines of 28 per cent. Thus, the decrease is most marked in the extreme ultraviolet. It

[133] Coblentz, W. W., Long, M., and Kahler, H., *J. Frank. Inst.*, **187**, 112 (1919); *Bureau of Standards Sci. Papers*, 330 (1918). Note also *Sci. Papers* 378 and 495.
[134] Nelson, H. A., *Proc. Am. Soc. Testing Materials*, **22**, II, 485 (1923).
[135] Reeve, L., *J. Phys. Chem.*, **29**, 39 (1925); Cunliffe, P. W., Franklin, R., Maddison, R., and Reeve, L., *Ibid.*, **30**, 1427 (1926).

was believed that for arcs employed in quantitative work in the region 2480 to 2890A, the energy distribution should be determined every 200 hours. The energy in this region was thought to be considerably reduced during the first 500 hours. The 2485A line sometimes disappeared within 100 hours and the 2300, 2340, 2370 and 2400A lines were ineffective after less than 50 hours. Similar observations were recorded by Gillam and Morton,[136] who believed that after a rapid fall in the output of the extreme ultraviolet in the first 150 to 200 hours, the output becomes fairly constant. After this first change, there occurs a slow nonselective loss in transmission of the burner. The first effect was thought due to the formation of SiO vapor inside the lamp and the second to the gradual deposition of a film of opaque silicon.

Hanovia lamps (Luxor B Alpine Sunlamp) are said to drop to 80 per cent of their initial emission in the first 300 hours, after which they remain fairly constant showing 73 per cent after 2000 hours.

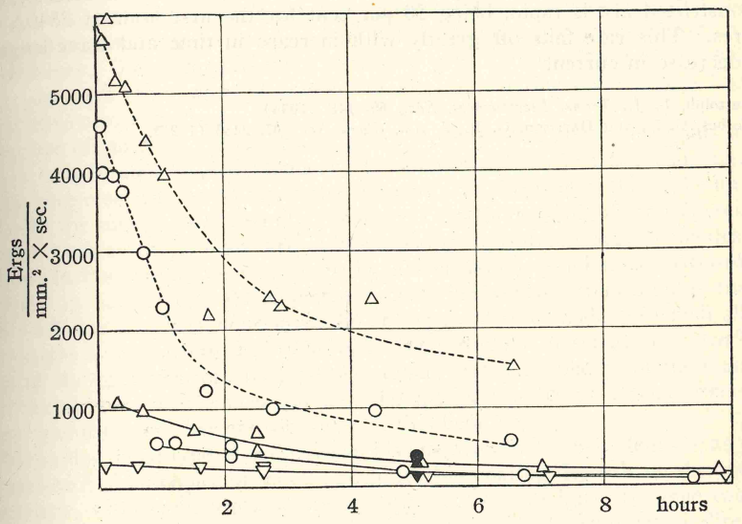


FIGURE 63. Rate of Deterioration of Constricted Lamp (Forbes and Harrison, *Journal American Chemical Society*).

Flynn [137] suggested that for a 220-volt lamp, an increase in the voltage at the rate of two volts per 100 hours of operation would compensate for the ageing loss.

Kolbert [138] proposed a circuit with variable resistance coil or tapped transformer and control switch marked on the dial so as to operate a lamp at 140, 150, 155, 160, 165 and 170 volts after 100, 250, 400, 600, 800 and 1000 hours, respectively. The manufacturers of the Uviarc recommended that during the first 500 hours the voltage be increased 3 per cent each 100 hours.

Devitrification in quartz plays only a secondary role in ageing, according to Meyn.[139] There is a black deposit on the inner surface, a part of which can be

[136] Gillam, A. E., and Morton, R. A., *Phil. Mag.*, **6**, 1123 (1928).
[137] Flynn, O. R., *Am. Dyestuff Reptr.*, **12**, 837 (1923).
[138] Kolbert, J. W., British P. 413,921, July 26, 1934, to British Hanovia Co., Ltd.
[139] Meyn, W., *Z. wiss. Phot.*, **25**, 345 (1927); *Brit. Chem. Abs.*, 677, B (1928).

rubbed off or removed by acids. Another deposit penetrated to a depth of 0.1 mm. and was thought to be either finely-divided mercury or elemental silicon. Buttolph has published a photomicrograph taken by Dr. Hodge of the Stevens Institute [140] of the inner surface of a glass tube of a mercury arc. The surface was densely and uniformly pitted. This probably occurs also in quartz tubes, increases with increased temperature, voltage or any other factor that increases bombardment by electrons or by mercury molecules or ions. In burners with tungsten anodes, sputtering of these has long been recognized as a factor in ageing. Figure 63 shows the rate of decline in energy per sq. mm. of exit slit of the constricted arc for three wave-lengths.[141] Inverted triangles indicate 4060A, upright triangles 3660 and circles 2540A. Dotted lines give the output of the constricted arc on 94 volts and 4.9 amperes, solid lines on 78 volts and 2.1 amperes. All intensities were multiplied by ten. The three blacked-in points indicate a new commercial arc on 82 volts and 4.1 amperes. A new constriction was inserted before the run with 2.1 amperes and this was cleaned and revitrified before that with 4.9 amperes. The deterioration of the constricted arc is rapid, being 50 per cent for the first hour at 2540A and 5 amperes. This rate falls off greatly with increase in time and wave-length and with decrease in current.

[140] Buttolph, L. J., *Trans. Electrochem. Soc.*, **65**, 148 (1934).
[141] Forbes, G. S., and Harrison, G. R., *J. Am. Chem. Soc.*, **47**, 2453 (1925).

Chapter 8

Mercury Discharge Lamps

Since the radiations from a mercury lamp are emitted from mercury vapor in the positive column, it is evident that, if mercury vapor is made to fill the lamp by vaporization from any reservoir, a mercury cathode is not essential. George [1] devised a lamp in which tungsten electrodes were used and the mercury was vaporized from a separate spherical bulb connected with the quartz tube by a narrow-bore tube. Before the lamp had heated up sufficiently to vaporize the mercury, the discharge was carried by an inert gas under pressure. George [2] stated that the ultraviolet output might be increased by using alternating current at high voltage and frequency. The terminals were connected with the inductance of an oscillating circuit, although other ways of converting local alternating current to a high frequency were also suggested.

The use of tungsten cathodes as a source for the emission of electrons at high voltages was limited by their tendency to sputter and blacken the lamp envelope. Greater progress was based upon the discovery by Wehnelt [3] that calcium oxide fused onto the surface of heated platinum forms a cathode of high electron emissivity at lower temperatures than are necessary for tungsten. Such cathodes were employed in the construction of lamps by Konen and Jungjohann.[4] According to Buttolph,[5] in more recent developments, nickel has replaced platinum as the base. Much work has also been done upon the development of cathodes in which alkaline-earth oxides with various additions have been applied to spirals of wire.[6] The theory of the operation of this type of cathode, and particularly, of the manner in which the physical or chemical union of the coating and base material affects satisfactory operation, lies beyond the scope of this book.[7]

The oxide-coated type of cathode can also be made with such elements as sodium and caesium.[8] The choice of metal and activating coating depends on the operating temperature, vapor pressure and other features of the design. In some cases, the oxide-coated cathodes are brought to the necessary cathode temperature directly by the cathode voltage drop and arc current. This is the arrangement in the low-voltage Cooper-Hewitt mercury rectifier lamp and in the high intensity mercury arc of the General Electric Vapor Lamp Co. In some cases, they receive a preliminary heating by a glow discharge facilitated by a starting gas. Because of the rather

[1] George H., U. S. P. 1,361,710 (1920); *J. Soc. Chem. Ind.*, **40**, 75A (1921).
[2] George, H., U. S. P. 1,671,109, May 29, 1928; British P. 234,834, March 18, 1926.
[3] Wehnelt, A., *Ann. Physik*, **14**, 425 (1904).
[4] Konen, H., and Jungjohann, W., *Verhandl. deutsch. Physik. Ges.*, **3**, 145 (1910).
[5] Buttolph, L. J., *Trans. Illum. Eng. Soc.*, **28**, 153 (1933); **30**, 151 (1935).
[6] Spanner, H. J., and Doering, U. W., British P. 397,162, Aug. 8, 1933; Meyer, F., and Spanner, H. J., British P. 274,027, Oct. 20, 1927; Germer, E., French P. 707,198, April 13, 1931; Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932; British P. 394,367 and 394,388; Spanner, H. J., Doering, U. W., and Germer, E., German P. 597,580, May 26, 1934.
[7] Dushman, S., *Rev. Modern Physics*, **2**, 381 (1930); Reimann, A. L., *Phil. Mag.*, **12**, 1073 (1931); Becker, J. A., *Phys. Rev.*, **34**, 1323 (1929); Druyvesteyn, M. J., and Warmoltz, N., *Physica*, **4**, 41 (1937); Suhrmann, R., and Frühling, G., *Naturwiss.*, **26**, 108 (1938).
[8] Becker, J. A., and Sears, W., *Phys. Rev.*, **38**, 2193 (1931); Benjamin, M., and Rooksby, H. P., *Phil. Mag.*, **15**, 810 (1933).

limited heat available for starting and for operation, the lamps are made as small and of as low a heat radiating and heat capacity as possible. In other lamps, the cathodes are separately heated by special elements. A number of cathodes have been described by Buttolph.[9]

The gas or metal vapor conducting arcs may be designed for the utilization of the emission of the radiations from the positive column, as in tubular lamps, or of that of the negative glow as in certain lamps of bulbular form. It is not possible to give an account of the many varieties of these lamps which have been proposed. Since much of the development of these lamps as ultraviolet sources has been intimately associated with the development of lamps for visible lighting, an historical account would involve much extraneous material. It is interesting to note that the development of modern gaseous conduction lamps has been based in large part upon the pioneering work of McFarlan Moore.[10]

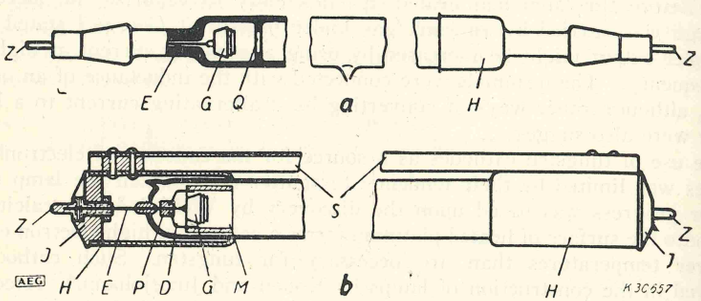


FIGURE 64. *a*. S, Burner of Quartz; *b*. S, Burner of I-G Phosphate Glass (Ende, *Z. technische Physik.*)

When the amount of mercury is such that no liquid or solid metal is present during operation of a lamp the static characteristic of the latter is not based upon the principles outlined in the previous chapters. Such lamps[11] are less affected by the temperature of the surroundings. As the load increases, the current increases markedly, but in contrast to the lamps described in Chapter 6 increase in voltage does not affect the operation of the lamp. The current can be adjusted by the series resistance rather than by ventilation, and the necessity for cooling is eliminated. The absence of the liquid mercury phase increases the stability of the lamp and also permits operation of the latter in any position. Bruijnes[12] pointed out that an excess of mercury might diminish the efficiency of a discharge tube by condensing on the walls and absorbing the ultraviolet. He described a discharge tube within which there was inserted a quartz tube. The latter was utilized to hold the material to be subjected to ultraviolet irradiation.

The lamp described by the Hanau Quarzlampen A.-G. uses special nickel-oxide-coated electrodes of basin-like members piled one on another. Argon at a few mm. pressure in the lamp serves to supply ions for conduction until the mercury, introduced as a small button of some hundredths of a gram sufficient to produce a vapor

[9] Buttolph, L. J., *Trans. Illum. Eng. Soc.*, **28**, 153 (1933); **30**, 151 (1935). See also Hull, A. W., *Trans. Am. Inst. Elec. Eng.*, **47**, 753 (1928); Found, C. G., and Forney, J. D., *Ibid.*, 747.

[10] Moore, McFarlan, *Gen. Electric Review*, **23**, 577 (1920).

[11] British P. 399,317, October 5, 1933, to Quarzlampen-Gesellschaft m.b.H., Hanau.

[12] Bruijnes, J., U. S. P. 1,994,301, March 12, 1935, to General Electric Co.

pressure of 700 mm. (corresponding to 350°C.), carries the discharge. Ignition is facilitated by the presence of a strip of Aquadag on the outside wall connected with the electrodes and interrupted in the neighborhood of one of them. This serves as a grounding device which collects electrostatic charges from the walls.[13] Very similar principles are employed in the therapy lamp (Alpina Heimsonne)[14] developed by that company. The therapy lamp is 10 to 20 cm. long and is enclosed in a special phosphate glass rather than in quartz. The glasses employed soften at 560°C. and, therefore, cannot stand the weight of masses of mercury but can be used with the self-igniting solid oxide electrodes which heat during the discharge. A millimeter of this glass transmits 34 per cent of the radiation of wave-length 2500A. When cool, the mercury condenses on the inner walls of the tube, the

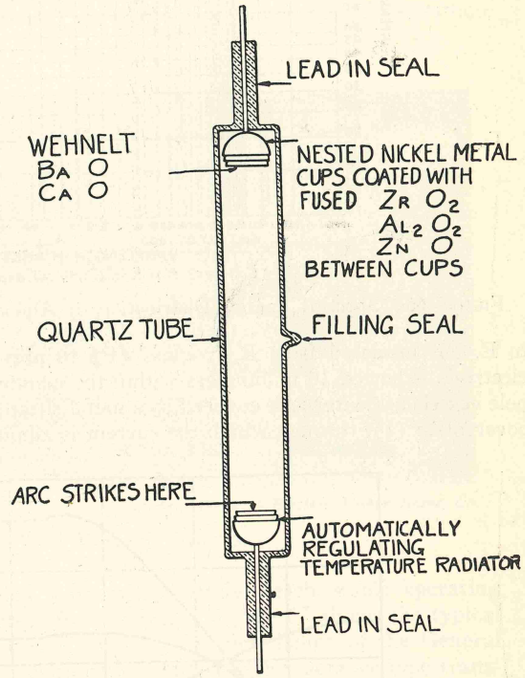


FIGURE 65.

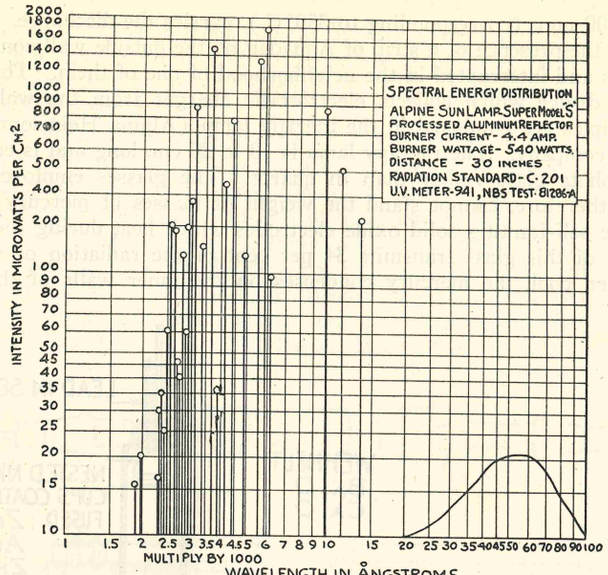
Quartz Burner Showing the Electrode Arrangement (Anderson and Bird, *Journal Optical Society of America*).

dimensions of which are so chosen that the discharge space is brought to 350°C. at its coolest spot, but nowhere exceeds 560°C. To secure this temperature, special pole-caps and metal protective mantles were placed about the electrodes to prevent the temperature of the glass in this region from approaching the softening point. The lamp is ballasted at 1.8 amperes, 120 volts burner tension for the 17 cm. arc, and worked at a point on the burner characteristic which, at 220 volts and 62 ohms, is still so far from the labile point that the discharge does not extinguish if the tension drops by 20 volts.

Figure 64 shows a section of the lamp. A glow electrode (G) sits on the sealed-in wire (E). The protective coat (M) is borne by two wires (D) joined

[13] See Spanner, H. J., U. S. P. 1,860,210, May 24, 1932.

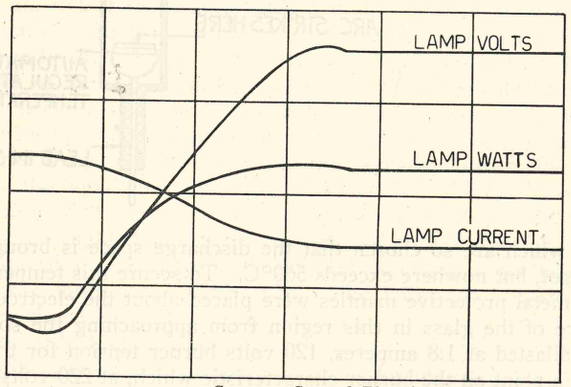
[14] Ende, W., *Z. tech. Physik*, **15**, 313 (1934).


SPECTRAL ENERGY DISTRIBUTION
ALPINE SUN LAMP-SUPER MODEL S
PROCESSED ALUMINUM REFLECTOR
BURNER CURRENT - 4.4 AMP.
BURNER WATTAGE - 540 WATTS.
DISTANCE - 30 INCHES
RADIATION STANDARD - C-201
U.V. METER-941, NBS TEST-81286-A
INTENSITY IN MICROWATTS PER CM2
MULTIPLY BY 1000
WAVELENGTH IN ÅNGSTROMS.

Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 66. Spectral Energy Distribution of Alpine Sun Lamp, Super Model "S."

to E, but insulated from E by glass (P) to prevent arcing to the mantle. The electrode is buried 10 millimeters within the mantle for better heat protection. The pole vessels are externally covered by a metal sheath (H), closed off by an insulating cover plate (I), through which the current is admitted, (Z). The two end sheaths



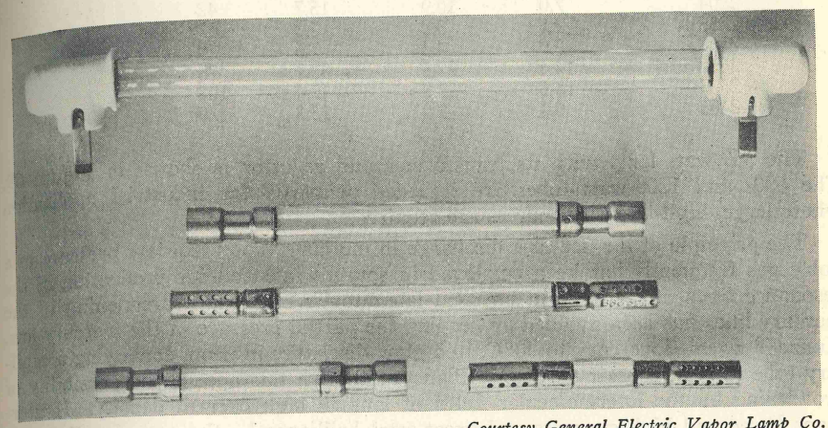
Courtesy General Electric Vapor Lamp Co.

FIGURE 67. Typical Starting Characteristics of 360-watt Uviarc.

are held by a long end-to-end shield which carries the whole burner. A transformer and accessory resistance are required. During starting, the voltage increases in proportion to the pressure for about six minutes, but there is a preliminary saddle

due to irregularities in heating up various parts of the tube before the arc burns steadily, after which the characteristic follows the usual hyperbolic curve.

Anderson[15] uses a laminated electrode structure comprising pieces of metal separated by barium and calcium oxides. This principle is employed in the more recent models of the quartz lamp of the Hanovia Co. (Figure 65). The heat is radiated directly from the electrodes, which consist of a number of nested metal cups connected electrically and mechanically by a weld, and separated by the oxide coatings which automatically regulate the temperature. The 200-watt burner operates on 220 volts a.c., has a diameter of 16 mm. and an arc length of 130 mm. A ballast resistance or reactance must be used in series to limit the current. The life of the lamp is about 2000 hours. The spectral energy distribution of an Alpine Sun Lamp (Super Model S) at a distance of 30 inches is given in Figure 66. There was a processed aluminum reflector. The burner current was 4.4 amperes and its wattage was 540.[16]



Courtesy General Electric Vapor Lamp Co.

FIGURE 68. New Mercury Uviarcs.

Lamps of the newer type, which start automatically, reach stable operating conditions within about three minutes after starting. Figure 67 shows the typical starting characteristic of the 360 watt Uviarc.[17] The new lamps of the General Electric Vapor Lamp Co. operate in conjunction with a high reactance type transformer. The reactance limits the discharge current, stabilizes the arc and minimizes the flicker in the radiation output. The transformer may also supply a leading current at relatively high voltage from an extension of the primary winding to a power factor correcting capacitor.

The lamps are supplied in five sizes (Figure 68) consuming 150, 250, 360, 600

[15] Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932; British P. 394,367 and 394,388; Anderson, W. T., Jr., U. S. P. 1,902,936, March 28, 1933; Anderson, W. T., Jr., and Bird, L. F., U. S. P. 2,006,081, June 25, 1935; *J. Opt. Soc. Am.*, **27**, 95 (1937). Note also Siemens and Halske, A.-G., British P. 475,763, Nov. 25, 1937; *Chem. Abs.*, **32**, 3279 (1938); Elenbaas, W., U. S. P. 2,116,741, May 10, 1938; *Chem. Abs.*, **32**, 4891 (1938).

[16] Personal communication, Hanovia Chemical and Manufacturing Co. See also Melville, H. W., *Trans. Faraday Soc.*, **32**, 1525 (1936).

[17] Unpublished data of Johnson, L. B., and Webster, S. B., communicated by the General Electric Vapor Lamp Co. See also Inman, G. E., and Lemmers, E., U. S. P. 2,085,530 and 2,085,531, June 21, 1937; *Chem. Abs.*, **31**, 5698 (1937).

and 1200 watts. The radiation outputs of these burners at various wave-lengths in microwatts per sq. cm. at one meter are given in Table 12.[18]

Table 12.—Radiation Output of Mercury Discharge Lamps.

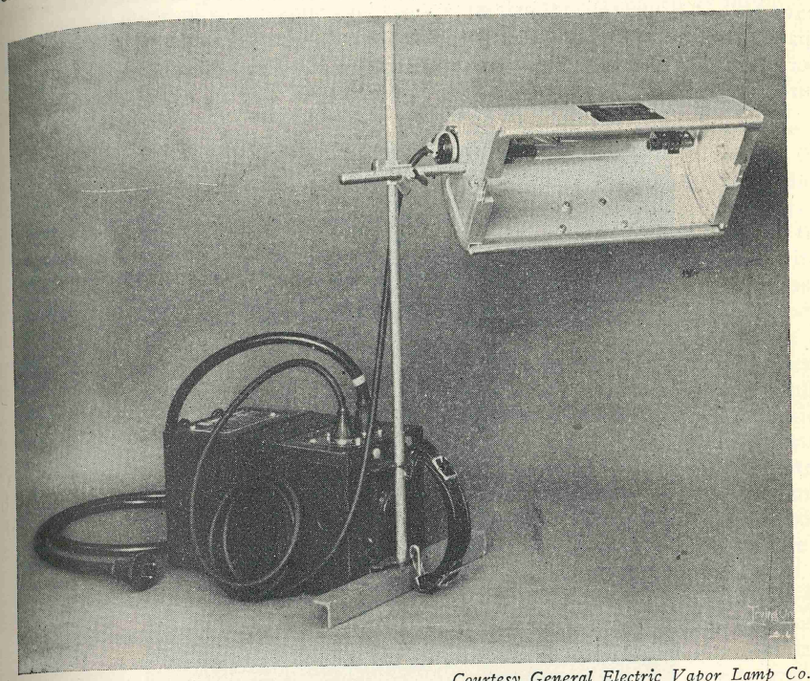
Wave-length (Ångströms)	Burner Watts: 150	250	360	600	1200
	Microwatts per sq. cm. at 1 meter				
5780	37.3	60.2	83	255	510
5461	33.5	56.0	82	222	445
4358	28.5	45.5	72	192	385
4047	16.9	26.8	45	111	223
3654	49.6	78.5	122	327	654
3341	5.3	7.4	11.6	35	71
3129	32.6	50.8	85	203	406
3022	16.6	25.3	39.4	107	214
2967	8.8	13.5	20.9	56	113
2894	3.5	5.3	8.3	23	47
2804	7.0	10.9	15.7	42	85
2753	2.5	3.8	5.5	17	33.6
2700	3.0	4.4	7.6	20	40.2
2652	14.4	22.5	83.1	88	176
2537	15.5	27.8	47.4	103	207
2483	6.1	9.9	13.3	39	79.5

The 360-watt lamp with its transformer and reflector is shown in Figure 69. The 600- and 1200-watt tubes are intended primarily for industrial application where large, high-intensity sources are required.

The principle of the use of a discharge in mercury vapor at a low pressure in a noble gas frequently has been employed in sources intended for production of the resonance lines of mercury in physical laboratories. Pressure broadening of the mercury lines has been avoided by keeping the partial pressure of the mercury low. Kunze [19] warmed mercury to 40°C. in a glow discharge in neon, employing a capillary tube to secure great surface brilliancy, although this opened the possibility of broadening by the intermolecular fields of ions in high current density. Houtermans [20] secured high currents and great total brilliance by the use of a discharge tube with oxide cathodes, employing argon at 3-4 millimeters. This form of discharge (studied by Pirani [21]) is characterized by high strength and line sharpness. The discharge was started by a small induction coil or a medical high-frequency apparatus, it being necessary only to bring the high-tension electrodes near the lamp. The temperature of the mercury reservoir was regulated by placing the reservoir in a side-tube dipped in water. One part of the illuminating tube was compressed into a flat rectangle 30 millimeters square and 2 millimeters thick to maintain the discharge against the quartz wall and so lessen the effects of self-absorption. The width of the discharge depended upon the current, increasing with the latter at constant current density, but never completely covering the area of the rectangle. When the lamp was started, there was at first a self-maintained discharge, showing a Faraday dark space. In this state, the voltage drop over the lamp was high (180-200 volts) and the current but a few milliamperes, the lamp remaining cold. At a certain current value, the oxide cathode began to emit strongly, the voltage dropped to between 20 and 30 volts and the current rose. The current was not

[18] Communication from the General Electric Vapor Lamp Co.
[19] Kunze, P., *Ann. Physik*, **5**, 793 (1930).
[20] Houtermans, F. G., *Z. Physik*, **76**, 474 (1932).
[21] Pirani, M., *Elektrotech. Z.*, **51**, 889 (1930).

permitted to rise above 3.6 amperes to prevent the oxide cathodes giving off a dust which blackens the tube. During starting, however, the resistance could be momentarily removed, permitting a current of 4 to 4.5 amperes. At 24 volts and 2.6 amperes, the intensity could be kept constant within 2 per cent for over two hours. Such lamps could be used for some hundreds of hours without deterioration.



Courtesy General Electric Vapor Lamp Co.

FIGURE 69. 360-watt Uviarc for General Laboratory Use.

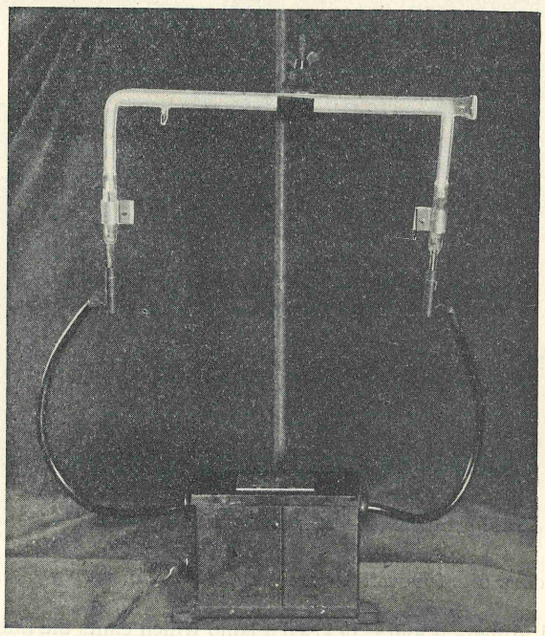
Kornfeld and Müller-Skjold [22] devised a lamp which emits the line 2537A twelve times as intensely as does the usual mercury arc. The lamp operates at 220 volts and has water-cooled tungsten electrodes. The cathode is coated with a mixture of barium and strontium carbonates and is heated with current from a step-down transformer.

The Hanovia Co. now supply tubes in which 85 per cent of the emitted light is at 2537A. They are built to consume 30-100 milliamperes at 2000 or more volts. With an input of 25 watts, they supply 40 microwatts of 2537A radiation per square centimeter at 20 inches. They are available in various forms, straight, U-shaped and S-shaped, and usually have a tube length of from one to six feet. A form intended as a source for work on the Raman effect is shown in Figure 70.[23]

In one of the first lamps of this type, Wiegand [24] employed a discharge in

[22] Kornfeld, G., and Müller-Skjold, F., *Z. physik. Chem.*, **B31**, 223 (1936).
[23] See Leighton, P. A., and Leighton, W. G., *J. Chem. Ed.*, **12**, 139 (1935).
[24] Wiegand, K., German P. 509,373, Nov. 4, 1926; U. S. P. 1,971,887, August 28, 1934, to Patent-Treuhand-Ges. für Elek. G.m.b.H.; *Chem. Abs.*, **28**, 6371 (1934).

nitrogen or carbon dioxide and some hydrogen at low pressures in a quartz or Uviol bulb containing a drop of mercury. The mercury extended the radiations from the limit of the nitrogen radiations (2800A) to about 2200A and improved the distribution of the spectral lines. The tube carried only 50 to 80 milliamperes, and operated at a temperature so low that it could be operated in direct contact with the material to be irradiated. Other forms, differing in structural features, have been described by Foulke,[25] who uses the negative glow between two closely spaced (0.5-2.0 mm.) oxide-coated nickel electrodes, in a gas containing neon (75 per cent) and helium (25 per cent) and a small quantity of argon at 30 mm. pressure. A small quantity of mercury is also present. The metastable potential of the



(Courtesy Hanovia Chemical and Manufacturing Co.)

FIGURE 70. Hanovia Sc-2537 Tube for Raman Work.

major component is to be greater than the ionizing potential of the minor component. This lamp, contained in a fused silica or Pyrex container fitted with a base plug, is operated on 100-110 volts direct current or 75 volts alternating current. As a "getter" it contains a bead of alkali-metal oxide, hydroxide or carbonate. The lamp may be used for therapy, photochemistry, or ultraviolet signaling.

The G-1 or Glow Lamp of the General Electric Co. consists of two oxide-coated tubular filaments heated from within by tungsten filaments, a connecting and supporting bridge and center support to hold them, and a pool of mercury. It produces ultraviolet radiation by virtue of a glow discharge in the mercury vapor at low pressure throughout the entire bulb. Consuming approximately 40 watts, the lamp

[25] Foulke, T. E., British P. 361,394, July 21, 1931, to the British Thomson-Houston Co., Ltd.; U. S. P. 1,990,174-5, February 5, 1935, to General Electric Vapor Lamp Co.

starts at a current of two amperes at 35 volts, and operates at 20 volts and two amperes. A separate small transformer is required for each lamp. It emits but little visible light.[26]

A number of lamps have been patented by the Philips Lamp Works. In one form[27] of positive column discharge of mercury in argon at 5 millimeters the electrodes are led out at one end of the tube. Two anodes are separated by a screen and the supply wires of the incandescent oxide cathode are surrounded by insulating envelopes. The tube is widened where the supply wires are taken out for mounting in a device for irradiating flowing substances. A quartz tube with graded seal is employed. In another form,[28] the operating current density is maintained so low, either by use of a suitable voltage and a resistance in series with the discharge, or by the use of a suitable gas filling, *e.g.*, argon, that the temperature of the tube is below 100°, and the vapor of the mercury contained in the tube is less than 0.3 millimeter pressure. A lamp has been described[29] in which the anodes are carbon cylinders with leveled-off ends. An inner concentric quartz tube for irradiation fluids is embodied in the apparatus. To prevent disintegration products of the cathode from settling on the walls, grid-shaped anodes of gauze or parallel wires stretched on a frame are used to attract disintegrating particles without seriously interfering with the passage of the rays.[30] Devers[31] proposed the use of a loose powder of nitrides of boron, zirconium or titanium to reduce the deposition of cathodic materials on the walls and to react with any trace of water vapor present. A device embodying a reflecting mirror of chromium on the inner wall of the tube is due to Zecher.[32] Reynolds[33] described an apparatus in which a high-tension discharge in mercury vapor in argon or neon occurs in a quartz tube free from external protuberances, which is to be immersed in the substance to be irradiated. There is an electrode at one end of a tube with a lead-in wire fused to another tube situated concentrically within the outer tube and fused to the latter. One electrode is of mercury, the other of tungsten or steel. The whole high-tension discharge is symmetrically placed and the radiations pass through only a single thickness of quartz.[34]

Garrett[35] described a glow lamp for ultraviolet radiation for clinical or household use operated on 110-220 volt alternating or direct current without auxiliary equipment. The radiations are emitted by a polyatomic gas such as nitrogen at 2-3 millimeters pressure in admixture with argon, neon and helium at 1-2 centimeters. It was stated that the monatomic gases alter the spectrum of the nitrogen, increasing the proportion of ultraviolet. The monatomic gases also function in starting the discharge and in keeping the operating potential relatively low. Con-

[26] See also Lederer, K. and E., German P. 600,757, July 31, 1934.

[27] N. V. Philips' Gloeilampenfabrik, British P. 320,358, October 9, 1928; French P. 662,717, October 20, 1928; *Chem. Abs.*, **24**, 270 (1930).

[28] British P. 299,704, October 22, 1928; N. V. Philips' Gloeilampenfabrik; *Brit. Chem. Abs.*, **B**, 246 (1930).

[29] British P. 299,931, November 8, 1928, to N. V. Philips' Gloeilampenfabrieken; *Chem. Abs.*, **23**, 3379 (1929).

[30] British P. 351,894, July 2, 1931, N. V. Philips' Gloeilampenfabrieken.

[31] Devers, P. K., U. S. P., 1,803,175, April 28, 1931.

[32] Zecher, G., U. S. P. 1,951,116, March 13, 1934; *Chem. Abs.*, **28**, 3279 (1934). See also British P. 381,084, September 29, 1932; 366,675, February 11, 1932, to Phillips Lamp Works.

[33] Reynolds, F., British P. 349,294, May 28, 1931.

[34] Many variations have been described. See, *e.g.*, Braselton, C. H., Ruben, S., Davies, L., and Harding, R., for a series of patents, U. S. P. 2,007,919-47, July 9, 1935, to Sirian Lamp Co.; Freedman, P., British P. 313,726-7, 1929; Geffcken, H., and Richter, H., British P. 265,636, May 3, 1928; Studienges. für Wirtschaft und Industrie, British P. 269,808, 1926; Kewley, F. E., and Balls, S. F., British P. 269,014, June 14, 1926. Even carbon electrodes have been proposed, British P. 410,706, 1934.

[35] Garrett, M. W., U. S. P. 1,783,643, Dec. 2, 1930, to Westinghouse Lamp Co.

centric grid-shaped electrodes of tungsten or molybdenum are employed in a quartz envelope, which contains also a strongly electropositive metal, alkali or alkaline-earth, which deposits on the electrodes and makes the lamp suitable for operation at 110 volts. Mercury may also be used in the lamp.

A low-pressure mercury glow-discharge lamp, employing indirectly-heated unipotential oxide-coated electrodes as the source of electron emission to ionize the mercury vapor has been described by Marden and Nicholson [36] of the Westinghouse Co. It is necessary to use a transformer or a ballast lamp with the glow lamp to avoid overheating the electrodes. The voltage across the terminals of the glow lamp, and the resultant heating of the electrodes, decrease to a certain extent with increasing glow current, making the device self-regulating. The electrodes serve alternately as anodes and cathodes when used on alternating current. Such lamps have been made in sizes from those taking 0.2 to 0.3 ampere in half-inch bulbs one inch long to 30-ampere models in bulbs 3 to 12 inches in diameter. Figure 71 shows

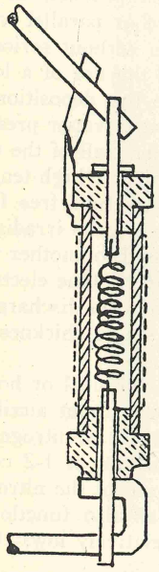


FIGURE 71 (Left).

Structure of Indirectly Heated Electrode of Marden and Nicolson. *(Transactions Illuminating Engineering Society).*

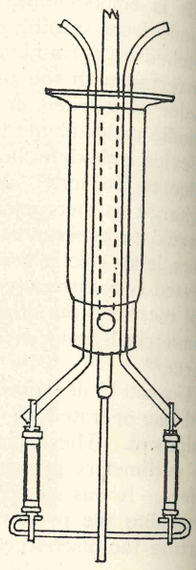


FIGURE 72 (Right).

Construction of Assembled Mount *(Transactions Illuminating Engineering Society).*

the indirectly heated electrodes and Figure 72 their mounting. The electrode around each heating coil is connected to the same lead-in wire as its respective coil. When the glow lamp is in series with a tungsten filament or other ballast on a 115-volt alternating current circuit, the voltage across the lamp is about 40 volts, until the electrodes are heated sufficiently to emit. During three to five seconds, the emission and glow-discharge increase and the lamp voltage drops to a point where the heating of the electrodes by the coils and by electronic and ionic bombardment maintains sufficient emission from the electrodes to sustain the glow-discharge current. During steady operation, about one-half of the current passes through the heater coils and the remainder is glow current. Marden and Nicholson gave data obtained with

[36] Marden, J. W., and Nicholson, M. G., *Trans. Illum. Eng. Soc.*, **26**, 592 (1931); British P. 374,466, May 21, 1930; *Chem. Abs.*, **27**, 3152 (1933).

a monochromator (uncorrected for reflection and absorption) comparing the energy distribution of the new glow lamp with those of the quartz mercury arc and the S-1 lamp. The percentage distribution of energy for the Corex glow lamp is about the same as for the mercury arc, except at the lower wave-lengths where the Corex glass absorbs the radiations. (See Chapter 10.) Of the total ultraviolet output, 90 per cent lies between 3132 and 2894A. On the other hand, Inman stated that, even through Corex, this glow lamp emits an amount of energy of the 2537A line which is undesirable for long-continued use. He believed that attempts to eliminate this would make the output between 2800 and 3100A negligible. Luckiesh pointed out that the S-1 lamp (see section on "dual-purpose" lighting) emits less of the 2537 line, since it operates under a higher pressure of mercury vapor.

Increasing the temperature or adding other gases such as argon concentrates the glow and diminishes the ultraviolet output. One, two, or possibly more of the lamps may be operated in series with a ballast which may be either a tungsten-filament lamp, an infrared heater, a choke coil, or a special transformer which can be concealed in a table lamp fixture.

Marden and Rentschler [37] claimed an improvement in the Marden glow lamp by making the heat-radiating capacity of the device great enough to maintain the internal temperatures between 20° and 75°C. The mercury reservoir is placed in a protuberance, with a more or less restricted opening, giving but a limited exposure of the mercury to the heat. This limits the mercury vapor pressure to 0.001-0.08 millimeter, which makes the emission of the 2537A line ten times as strong as the other lines. This point has also been emphasized by the Philips Lamp Works.[38] The desirability of increasing the output of this line obviously depends upon the purpose to which the lamp is to be put, a matter which will receive attention in subsequent parts of this book.

Prouty [39] described a portable compact power system including transformers, milliammeters, etc., for operating several quartz discharge tubes at high voltages and low currents (30-50 milliamperes). The tubes are of small diameter to reduce self-absorption of the resonance lines and yield intense short-wave ultraviolet radiations stated to be applicable for dental and surgical utilization.

Ultraviolet-emitting discharge tubes of quartz employing other emitting metals than mercury have been produced; sodium and magnesium have been proposed. Magnesium tends to impair the transparency of the tube. The Philips Works [40] proposed to preserve the transparency of the walls by coating that part of the wall intended for the passage of the rays with a substance (potassium chloride or fluoride or fluoborate in the case of magnesium) which either prevents deposition of the metal or renders the deposit transparent to the rays desired. Calcium fluoride may be used as a coating for the interior of a mercury vapor lamp. When the tube contains sodium vapor, the wall may be coated with sulfur or phosphorus. de Boer [41] places on some non-transmitting part of the bulb, a material which will adsorb the depositing substance and liberate it on heating. Carbon, calcium fluoride or zirconium oxide are suggested. The spectrum is emitted by iodine vapor in this tube.

[37] Marden, J. W., and Rentschler, H. C., U. S. P. 1,917,848, July 11, 1933. See also Canadian P. 355,173., Jan. 7, 1936. For more recent developments, see Marden, J. W., and Meister, G., U. S. P. 2,129,357, Sept. 6, 1938; *Chem. Abs.*, **32**, 8285 (1938).

[38] British P. 299,704, January 16, 1930, to N. V. Philips' Gloeilampenfabrieken.

[39] Prouty, W. O., U. S. P. 1,965,947, July 10, 1934; U. S. P. 2,093,735, Sept. 21, 1937; *Chem. Abs.*, 31, 7773 (1937). See also Le Bel, C. J., U. S. P. 2,126,787, Aug. 16, 1938; *Chem. Abs.*, **32**, 7836 (1938).

[40] British P. 336,222, July 5, 1929; 356,407, September 10, 1931; both to N. V. Philips' Gloeilampenfabrik.

[41] de Boer, J. H., U. S. P. 1,935,699, November 21, 1933; *Chem. Abs.*, **28**, 693 (1934).

For mercury vapor, gold foil may be used. de Groot and Reerink [42] employ a member acting as a chimney above the path of discharge to carry off the vapor, which may settle on or combine with the chimney, a part of which is of gauze. This chimney is to be employed in a magnesium vapor lamp.

Tubes have been described in which the emission of ultraviolet radiations is caused by bombardment by electrons of a fluorescent substance on the electrodes or in a very thin film on the inner side of the wall of the quartz tube. Sulfides, selenides, oxides of the alkali or alkaline earth metals, boron compounds, etc., with small amounts of iron or mercury compounds incorporated, serve as emitters. Yttrium, lanthanum and gadolinium compounds increase the emission. The tube has a very low pressure gas or vapor filling. A grid-like anode accelerates the electrons emitted by the cathode. Visible radiations are emitted by the wire of the heater. A chromium or magnalium film on the opposite part of the bulb serves as a mirror.[43]

Materials within the envelopes of discharge tubes may also be excited by ultraviolet rays within the tubes to give blue or white fluorescent light.[44] In some of these zinc silicate, calcium tungstate and calcium molybdate form the internal coatings of the envelopes. A series of variously fluorescing layers is sometimes used. Fluorescent glass envelopes may also be employed.[45] Rare gas fillings [46] are sometimes used to the exclusion of mercury.[47]

Dual-Purpose Sources

The proportion of the health-giving ultraviolet in the sun's radiations is small and varies greatly with the seasons and atmospheric conditions. It is greatly lessened by dust and smoke, so that in industrial communities and in cities very little may be available. Means have been developed for so altering the ordinary sources of illumination of homes, hospitals, schoolrooms, gymnasia, etc., as to enable them to provide also a supply of the desirable ultraviolet radiations. Illumination by such sources has come to be known as "dual-purpose" illumination, *i.e.*, visible illumination and simultaneous ultraviolet irradiation.

The engineering problems are concerned with the design and construction of a reasonably-priced source of ultraviolet within a lamp bulb supplying visible light

[42] de Groot, W., and Reerink, E. H., U. S. P. 1,905,688, April 25, 1933, to General Electric Co.

[43] Hummel, C., British P. 387,130, Feb. 2, 1933; Aicher, J. D., U. S. P. 2,109,984, March 1, 1938; *Chem. Abs.*, **32**, 3279 (1938); French P. 828,067, May 10, 1938, to Compagnie des lampes; *Chem. Abs.*, **32**, 6962 (1938).

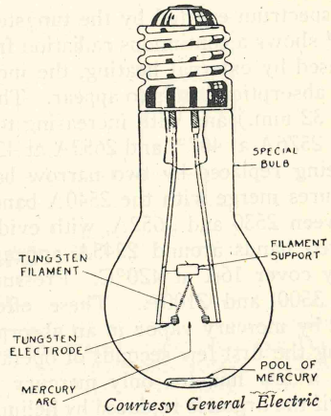
[44] British P. 459,323, Jan. 6, 1937; 473,929, Oct. 22, 1937; *Chem. Abs.*, **32**, 2854 (1938); German P. 656,213, Feb. 1, 1938; British P. 476,240, Dec. 7, 1937; 485,875, May 26, 1938; *Chem. Abs.*, **32**, 8286 (1938), all to Patent-Treuhand-Ges. für elektrische Glühlampen. See also Randall, J. T., British P. 466,503, May 28, 1937; *Chem. Abs.*, **31**, 7774 (1937); British P. 469,731-2, July 27, 1937; *Chem. Abs.*, **32**, 436 (1938), to General Electric Co., Ltd. Breadner, R. L., Randall, J. T., and Ryde, J. W., British P. 474,298, Oct. 28, 1937; *Chem. Abs.*, **32**, 2854 (1938); Randall, J. T., British P. 474,457, Nov. 2, 1937; *Chem. Abs.*, **32**, 2854 (1938). Rhodamine dyes may also be used, according to McKeag, A. H., and Randall, J. T., British P. 474,297, Oct. 28, 1937; *Chem. Abs.*, **32**, 3279 (1938); Jenkins, H. G., Ryde, J. W., and Wilson, G. H., British P. 483,846, April 27, 1938; *Chem. Abs.*, **32**, 6961 (1938); Jenkins, H. G., Canadian P. 375,310, July 26, 1938; *Chem. Abs.*, **32**, 6962 (1938); Randall, J. T., Canadian P. 375,308, July 26, 1938; *Chem. Abs.*, **32**, 6962 (1938).

[45] French P. 808,048, Jan. 27, 1937, to Corning Glass Works; *Chem. Abs.*, **31**, 6434 (1937); British P. 476,945, Dec. 20, 1937, to I.G. Farbenindustrie, A.-G.; *Chem. Abs.*, **32**, 4298 (1938); British P. 484,975, May 12, 1938, to N. V. Philips' Gloeilampenfabriken; *Chem. Abs.*, **32**, 8286 (1938).

[46] French P. 810,298, March 18, 1937; *Chem. Abs.*, **31**, 8384 (1937); British P. 474,907, Nov. 9, 1937; *Chem. Abs.*, **32**, 3280 (1938); French P. 822,815, Jan. 8, 1938; British P. 457,317; *Chem. Abs.*, **31**, 2946 (1937); all to Soc. anon. pour les applications de l'electricité et des gaz rares-etablissements Claude-Paz and Silva. Laise, C. A., U. S. P. 2,116,977, May 10, 1938; *Chem. Abs.*, **32**, 4892 (1938); Fritze, O., Rüttenauer, A., and Wiegand, K., U. S. P. 2,103,032, Dec. 21, 1937; *Chem. Abs.*, **32**, 1193 (1938).

[47] For general discussions of this new type of fluorescent lighting which has the advantage of simulating daylight, see Claude, G., *Compt. rend.*, **203**, 1203 (1936); Servigne, M., *Ibid.*, 1247; Harrison, W., and Hibben, S. G., *Elec. World.*, **109**, 1530 (1938); Inman, G. E., and Thayer, R. N., *Elec. Eng.*, **57**, 245 (1938); von Ardenne, M., *Z. tech. Physik*, **19**, 41 (1938); Hibben, S. G., *Elec. J.*, **35**, 269 (1938).

and capable of operating from an ordinary lamp socket without the necessity of elaborate or expensive accessory equipment. From a therapeutic standpoint, the questions of wave-length range and intensity are paramount. It is necessary to choose for the envelope of the lamp bulb a material which will transmit visible light and ultraviolet radiations longer than about 2900 to 3000A and absorb those shorter than this limit, since the shorter rays are known to exhibit deleterious effects. As it is well known that excessive exposure to the sun's ultraviolet transmitted by the earth's atmosphere (longer than about 2950 to 3000A) may be harmful, it is necessary that the ultraviolet radiations emitted by a "dual-purpose" lamp be low in intensity since the lamps are used for considerable periods in ordinary home illumination. This explains the otherwise paradoxical nature of the claims of certain manufacturers that their bulbs emit only very low intensities of ultraviolet. A considerable field remains to be explored in order that the most suitable intensities and wave-length regions for effecting desired therapeutic ends may be firmly established. It is important that exact data be acquired regarding the effects of prolonged exposures to low intensities of the therapeutic range of the ultraviolet. Comparatively small amounts seem to be needed, at least for the prevention of rickets in chickens.[48] An industrial Cooper-Hewitt arc in glass affords some antirachitic protection, although not as much as one in Corex D glass, which, in turn, is somewhat less effective than one in quartz. Even 60- or 500-watt Mazda CX lamps, which have only a small ultraviolet output, have been recommended for long-continued use in poultry houses.[49]



Courtesy General Electric Co.

FIGURE 73.

Sunlight (Type S-1) Lamp.

One of the first bulbs for "dual-purpose" lighting was the S-1 sunlamp.[50] It comprises a combination of a mercury arc in argon between tungsten electrodes and an incandescent tungsten lamp in the same bulb, the latter of special glass of low iron content to transmit radiations from 2800 to 3100A.[51] Figure 73 shows the

[48] Hughes, J. S., and others, [*Trans. Ill. Eng. Soc.*, April, 1927]; cited by Buttolph, L. J., *Trans. Ill. Eng. Soc.*, **26**, 583 (1931).

[49] Anon., *Trans. Ill. Eng. Soc.*, **26**, 551 (1931).

[50] Luckiesh, M., *Gen. Electric Rev.*, **33**, 89 (1930); Forsythe, W. E., *et. al.*, *Gen. Elec. Rev.*, **33**, 358 (1930); Luckiesh, M., *Elec. World*, **94**, 835 (1929); **95**, 300 (1930); *Trans. Ill. Eng. Soc.*, **25**, 397 (1930); Gordon, N. T., and Benford, F., *Gen. Elec. Rev.*, **33**, 283 (1930); Forsythe, W. E., and Christison, F., *Ibid.*, **32**, 662 (1929).

[51] Strickland, R. F., British P. 147,292, 317,832, 375,477 (1932), to British Thomson-Houston Co., Ltd. Strickland, F., Blake, H. D., and McLean, S., British P. 398,290, September 14, 1933. See also British P. 383,342, November 17, 1932, to Zaidan-Hojin Aoyagi Kenkyusho, for a method of starting a similar lamp.

structures within the bulb. No tilting is required to start this lamp. When the filament is lighted, the arc strikes across the filament terminals and disposes itself across the main electrodes. A wide range of operating angles is possible. A low-voltage supplied by a transformer with a special volt-ampere characteristic is essential to the operation of this lamp, which consumes approximately 400 watts. The no-load voltage of the secondary of the transformer is approximately 35. When the switch is closed, the filament takes about 9 amperes and the drop across it is about 33 volts. The mercury arc starts in parallel, the voltage drops to eleven volts, and the total current through both arc and filament is 30 amperes. In operation, the arc supplies about one-fourth of the light, two-thirds coming from the tungsten electrodes, the color temperature of which is above 3500°K. The lamp is said to be twenty times more effective than summer sunlight. A frosted bulb is used, and the coiled filament is inverted and located above the electrodes. In another model, S-2, the arc length is increased, and a metal cap of aluminum is placed over the lower portion of the bulb to minimize glare and to redirect much energy back into the mercury vapor area, increasing the operating temperature. As a result, the lamp emits about one-half as much ultraviolet as the S-1 model, while consuming only 40 per cent as much energy. The lives of the S-1 and S-2 lamps are shortened by both over- and under-voltage operation.[52] Porter, Egeler and Sturrock[53] have tabulated electrical and other physical data regarding these sources. Luckiesh has pointed out that the high mercury-vapor pressure of these lamps leads to a high degree of absorption of the 2537A line, long-continued exposure to which would be dangerous.

The spectrum emitted by the tungsten-mercury arc, according to Forsythe and Easley,[54] shows a continuous radiation from 4000 to 2100A. When the temperature is increased by external heating, the increased mercury vapor pressure causes the mercury absorption bands to appear. The 2540 band is 0.1A wide at 220°C. (vapor pressure 32 mm.) and with increasing temperature spreads to longer wave-lengths, reaching 2576A at 407°, and 2652A at 426°C. At 350°C., the resonance line disappears, being replaced by two narrow bands at 2534 and 2532A which at higher temperatures merge with the 2540A band. At 426°C., there is continuous absorption between 2530 and 2652A, with evidence of further absorption beyond 2652A. Five fluted bands around 2345A appear between 320° and 340°C. and broaden until they cover 16A at 420°C. Pressure causes the disappearance of some lines between 3500 and 2100A. These effects are somewhat different from those exhibited by mercury vapor in an absorption cell.

During the first few seconds of operation, the S-1 lamp emits some argon lines, but after a few minutes only mercury lines are detected.[55] Similar effects are observed if the argon is replaced by helium, neon, nitrogen or carbon dioxide. When hydrogen is the gas present, the lamp continues to radiate bands characteristic of mercury hydride, along with several other bands at shorter wave-lengths.

Other data on the radiations emitted by the General Electric Sunlamp have been published by Benford,[56] Coblentz [57] and Barnes.[58] Barnes gave the average energy flux values of a number of lamps for the principal mercury lines between 2500 and

[52] Oday, A. B., and Porter, L. C., *Trans. Ill. Eng. Soc.*, **28**, 121 (1933).
[53] Porter, L. C., Egeler, C. E., and Sturrock, W., *Trans. Ill. Eng. Soc.*, **27**, 23 (1932).
[54] Forsythe, W. E., and Easley, M. A., *Phys. Rev.*, **36**, 150 (1930).
[55] Dooley, D., *Phys. Rev.*, **36**, 1476 (1930).
[56] Benford, F., *J. Motion Picture Eng.*, **14**, 414 (1930); Gordon, N. T., and Benford, F., *Gen. Electric Rev.*, **33**, 290 (1930).
[57] Coblentz, W. W., *J. Am. Med. Assn.*, **95**, 411 (1930).
[58] Barnes, B. T., *Phys. Rev.*, **36**, 1468 (1930).

6000A, and for the continuous spectrum up to 17,000A, determined by thermopiles and galvanometer, with a quartz prism monochromator which received on its slit energy from all parts of the arc and the electrodes. The line and continuous emissions were separated by taking readings both at the lines and at intermediate points, plotting continuous curves from the latter, and deducting the continuous curves from the values taken at the lines. The continuous curve was possibly too high below 4500A because of the inclusion of less important mercury lines, while the opposite was true in the red and infrared regions.

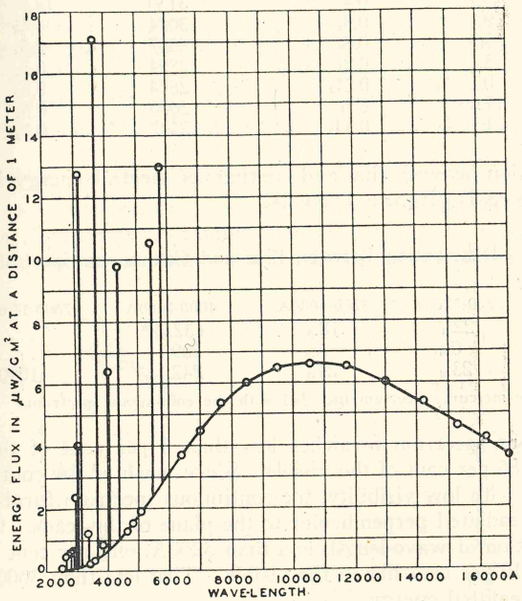


FIGURE 74. Energy Flux (μw/cm^2) One Meter from Center of Arc (General Electric Sunlamp) in a Direction Normal to the Plane of the Leads. Lamp burning without reflector with 115 volts on the primary of the transformer. Average lamp current and voltage 30.9$_5$ amps. and 10.6 volts. Curve represents energy in 50A band of continuous spectrum. Heavy lines above the curve give energy flux in lines or groups of lines in arc spectrum (B. T. Barnes, *Physical Review*).

In Figure 74 the intensities in microwatts per square centimeter at one meter distance in a direction perpendicular to the plane of the leads are given for an average of 26 lamps, operated with 115 volts on the primary of the transformer. The peak of the curve lies at about 10,600A, quite close to the maximum in the curve for the energy radiated by tungsten at 2500°K. The shape of the curve below 5000A, however, is approximately that for tungsten at 3250°K., the temperature of the hottest parts of the electrodes. The output of visible and ultraviolet radiations was much too high in comparison with that of the infrared for tungsten at 2500°K., a fact explained by the composite nature of the continuous radiation, the electrodes (above 3000°K.) giving a relatively high proportion of visible and ultraviolet, while the filament and the incandescent parts of the leads at much lower temperatures,

but with a larger area, give much of the infrared, and shift the maximum to longer wave-lengths.

The average total energy flux at one meter is 2380 microwatts per square centimeter (10.6 volts and 30.95 amperes). Table 13 gives the average energy flux for each of the principal mercury lines, and the corresponding per cent of the average total energy flux.

Table 13.—Energy Flux of Mercury Lines.

Wave-length of line, A	Microwatts per cm.²	% of total	Wave-length of line, A	Microwatts per cm.²	% of total
5780	9.7	0.4	3130	13.5	0.5_7
5461	8.2	0.3_4	3024	4.4_0	0.1_9
4358	9.0	0.3_8	2967	2.5_4	0.10_7
4047	5.8	0.2_5	2894	0.7_1	0.03_0
3905	0.4	0.01_7	2804	0.6_9	0.02_9
3650	17.4	0.7_3	2650	0.6_5	0.02_7
3342	1.1	0.04_6	2537	0.1_2	0.00_5

The distribution between line and continuous spectral energy in various broad wave-length regions is given in Table 14.

Table 14.—Distribution Between Line and Continuous Spectral Energy.

Microwatts per cm.²	2500-3200A	3200-4000A	4000-7600A	7600-17,000A	17,000A
Line spectrum	22.6	18.9	(32.7)*	....	....
Continuous	0.6	5.2	209.	....	....
Both	23.2	24.1	242.	1090	1000

* Red lines in the mercury spectrum included with the continuous spectrum.

The continuous spectrum furnishes less than 3 per cent of the energy below 3200A, but over 86 per cent of the visible. Since much of the continuous spectrum is in the red end with low visibility, the continuous spectrum furnishes only 76 per cent of the light radiated perpendicular to the plane of the leads. Of the total, one per cent is radiation of wave-length less than 3200A, one per cent is between 3200 and 4000A, and 10 per cent lies in the visible. That less than 3000A is only 3 per cent of the total emitted energy.

The results are in fair agreement with those of Benford, although the compositions of the bulbs have been changed. Different lamps vary widely in regard to the emission of the 3650A line, the intensity of which often increases over 50 per cent during the first 40 hours of burning. Benford found 28 per cent higher values for the energy between 4000 and 7000A (185 microwatts per square centimeter), a divergence for which no explanation could be given. The results are not comparable with those of Coblentz whose measurements were made upon the whole lamp unit, including a reflector. Under these conditions, the temperature of the mercury pool is 7° higher and the output below 3200A might be expected to be 10 to 15 per cent greater.

There have been other types of lamps proposed for "dual-purpose" lighting. The bulb of Corex (or Pyrex) may contain a mercury globule and oxide-coated electrodes to produce the ultraviolet-emitting glow discharge that fills the bulb at low temperature, while a sealed inner bulb provided with a tungsten filament serves both as a ballast resistance for the mercury vapor discharge and as a source of light.[59]

[59] Inman, G. E., British P. 390,384, April 6, 1933, to British Thomson-Houston Co., Ltd.

[60] Oosterhuis, E., U. S. P. 1,951,106, March 13, 1934, to General Electric Co. See also Craig, P., U. S. P. 1,798,658, March 31, 1931.

Oosterhuis[60] has described a reading lamp, with a standard containing the necessary transformers, which may comprise a helically wound glower for infrared and visible light, ultraviolet being supplied by a discharge between an incandescent cathode and two anodes in argon at a few millimeters, the tube containing some liquid mercury. The two sources employ separate circuits, each with a transformer, and are usable independently. Sperti[61] placed the arc and the filament in separate chambers.

Other attempts to produce "dual-purpose" illumination include utilization of a combination of separate quartz mercury arcs of usual form, and lamps for visible light in one fixture, provided with reflectors, filtering windows, and provisions for ventilation.[62] There has also been a considerable development of reflectors and accessory fixtures for the application of the S-1 Sunlamp. Oxidized or polished aluminum and polished chromium are among the more effective reflecting materials for ultraviolet between 2800 and 3200A.[63] Details of installations for homes, schools, offices, gymnasia, swimming pools, etc., have been described.[64]

Metallic Vapor Arcs Other Than the Mercury Type

The dependence of the intensity and efficiency of radiation in metal vapors on pressure is similar for mercury, cadmium and zinc.[65] At the time of the development of the mercury-vapor arc, Stark and Küch[66] examined Heraeus quartz lamps

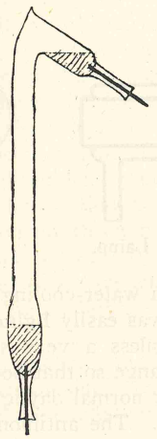


Figure 75.

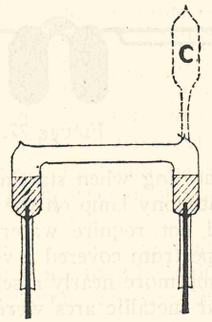


Figure 76.

having electrodes of metals and metalloids. The lamps were made in both of the forms indicated by Figures 75 and 76. Most of these lamps are of little practical interest because of the difficulty of starting, although developments of the cadmium

[61] Sperti, G., British P. 396,210, August 3, 1933.

[62] Rolph, F. W., U. S. P. 1,945,567, February 6, 1934, to Holophane Co. Paget, R. A. S., U. S. P. 1,943,877, January 16, 1934, to Thermal Syndicate.

[63] Coblentz, W. W., and Stair, R., *Bureau Standards J. Res.*, **4**, 189 (1930); Luckiesh, M., and Taylor, A. H., quoted by Porter, L. C., Egeler, C. E., and Sturrock, W., *Trans. Ill. Eng. Soc.*, **27**, 30 (1932).

[64] Oday, A. B., and Porter, L. C., *Trans. Ill. Eng. Soc.*, **28**, 121 (1933).

[65] Fabrikant, V. A., *Bull. acad. sci. U.R.S.S., Classe sci. math. nat. Ser. phys.*, 441 (1936); *Chem. Abs.*, **31**, 2925 (1937).

[66] Stark, J., and Küch, R., *Physik. Z.*, **6**, 438 (1905).

arc have excited interest. The outer diameter was 0.9 centimeter, the length of the form shown in Figure 75 was 13 centimeters and of that shown in Figure 76 was 9 centimeters. Nickel rods served to conduct the current to anode and cathode. The lamp was charged with metal by means of the container C shown in Figure 76. This container was filled with molten metal and on evacuation of the tube the metal passed into the lamp tube, after which the container C could be removed by fusing the narrow part. The lamp was pumped out thoroughly while in operation in order to get a satisfactory vacuum. The lamp was started by a spark from an induction coil, the metal being heated by a gas blast-lamp until sufficient metal vapors had been produced to cause an arc to form. A voltage of 100-200 was used.

The cadmium lamp was easy to start and operated at 2 to 5 amperes with metal-cooling; with water-cooling it could be operated at 8 amperes. The zinc lamp was more difficult to start and required heating with a blast lamp in order to put it into operation. With metal-cooling it operated at 3 to 5 amperes. The lead lamp required very intense heating in order to start. With water-cooling it operated at 8 to 10 amperes producing a strikingly rich spectrum. The bismuth lamp also

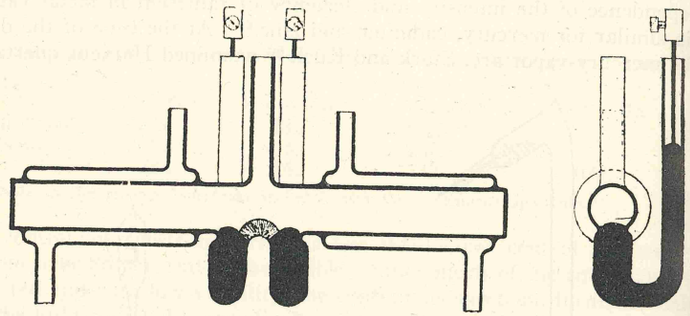


FIGURE 77. Cadmium Lamp.

required intense heating when starting and with water-cooling could be run at 7 amperes. The antimony lamp on the contrary was easily lighted and burned at 3 amperes, and did not require water-cooling unless a very strong current was employed. The spectrum covered a very wide range so that bodies exposed to the light from this lamp more nearly resembled their normal daylight color than when mercury or similar metallic arcs were employed. The antimony arc gave rise to very strong fluorescent effects, sodium glass fluorescing strikingly with a greenish-yellow color, while lead glass exhibited a blue fluorescence. Tellurium and selenium lamps were also tested. The former was operated at 6 amperes. The selenium lamp offered difficulties in starting. A form of cadmium arc lamp, that of Lowry and Abram,[67] shown in Figure 77 maintains the arc between water-cooled electrodes of solid cadmium. This cooling is important, partly because it checks the vaporization of the metal, but mainly because if the metal is allowed to melt it is liable to crack the tube whenever the lamp is started or stopped.

The lamp is operated in conjunction with a Gaede pump, as the metal gives off considerable quantities of gas under the influence of the electric discharge, and this gas must be pumped off in order to maintain the vacuum. Occasionally, when the

[67] Lowry, T. M., and Abram, H. H., *Trans. Faraday Soc.*, **10**, 103. Note Bates, F. J., *Phil. Mag.*, **39**, 353 (1920).

vacuum is good, the arc will start itself on merely switching on the current, but usually it is necessary to start the arc by a spark. This can be done conveniently by connecting the electrodes to the inner walls of two Leyden jars and connecting the outer walls to the secondary terminals of an induction coil. The light emerges through two windows of quartz. In one form of the lamp these windows are protected from condensed metal by water-jacketing the ends of the tube to which they are attached, but the water-jacketing must not extend to the central part of the tube. The latter must remain hot in order to prevent the formation of a conducting bridge of condensed metal. An arch of silica is provided to bring the arc to the center of the tube. The cadmium arc will burn quite well under a pressure of 100 volts, but it has a longer life if the voltage is higher, owing to the fact that an arc of greater length can be kept alight. The extinction of the lamp on the lower voltages is caused most frequently by the distillation of cadmium from the electrodes, which thus become shortened unduly.

Stammreich [68] describes a metallic vapor lamp using cadmium amalgam in which a condenser is connected to the arc tube for collecting metal distilled from the latter. In some instances [69] mercury may be distilled from the amalgam to a separate compartment which is then closed before the cadmium begins to vaporize. The mercury is afterward run back by tilting the lamp.

Nagaoka and Sugiura [70] have reviewed the development of cadmium lamps with emphasis on the deficiencies of the previous types. They describe a lamp which comprises a tube with fused quartz cylinder surrounded with molybdenum or tungsten wire, the latter heated by electric current which can be raised to the required temperature. A second fused quartz cylinder is placed above the first cylinder, suspended by a holder which has a hole permitting light to pass through a window placed at the end of the side arm. The cadmium vapor is produced in this cylinder. The luminous particles can be concentrated in a second cylinder to obtain great intensity of light and the density of the cadmium vapor can be controlled by heating the coil around the first cylinder. A cathode of coiled tungsten is used to concentrate electronic currents through the cadmium vapors toward the molybdenum anode. Electric potential of 100 volts and electronic current of 0.3 to 4 amperes between cathode and anode are sufficient to excite cadmium vapors at 300° and to obtain intense and stable light. The tube is constructed of double glass and is water-cooled.

Other cadmium amalgam discharge tubes have been described by the N. V. Philips' Gloeilampenfabriken.[71] Krishnamurti [72] has found a cadmium-tin alloy arc a suitable source for the excitation of Raman spectra. The lines 5085.8 and 6438.5A are particularly effective.

Because of its wider spectral extension in the visible, the cadmium-mercury vapor lamp has attracted much attention for general illumination, but this is not within the province of this book.[73]

A drawback to the use of cadmium- or zinc-enclosed arcs has been their short-

[68] Stammreich, H., British P. 294,172, July 19, 1927.

[69] Stammreich, H., French P. 657,426, July 11, 1928; U. S. P. 1,828,346, October 20, 1931.

[70] Nagaoka, H., and Sugiura, Y., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **10**, 263 (1929); *Chem. Abs.*, **23**, 5118 (1929).

[71] British P. 336,208, July 5, 1929, to N. V. Philips' Gloeilampenfabrieken; Elenbaas, W., Canadian P. 371,090, Jan. 11, 1938; *Chem. Abs.*, **32**, 2854 (1938); Elenbaas, W., and Jonas, G. B., U. S. P. 2,116,742, May 10, 1938; *Chem. Abs.*, **32**, 4891 (1938).

[72] Krishnamurti, P., *Indian J. Physics*, **5**, 587 (1930). *Chem. Abs.*, **25**, 1159 (1931).

[73] Spanner, H. J., *Trans. Illum. Eng. Soc.*, **30**, 178 (1935); *Chem. Abs.*, **29**, 5359 (1935). For a general discussion of recent electric vapor lamps, see Malley, R. D., *Elec. Eng.*, **53**, 1447 (1934), and Marden, J. W., Beese, N. C., and Meister, G., *Trans. Illum. Eng. Soc.*, **32**, 84 (1937).

ness of life. The metals even when pure tend to adhere to the walls, and break the latter on cooling. Bates [74] found the addition of a small proportion of gallium to lessen this tendency in the case of cadmium. As he found it difficult to obtain pure gallium, he later employed tin instead, using a 50-per cent alloy of cadmium and tin, which melted at 176-200°C.[75] The arc used was of the Cooper-Hewitt type; the low vapor-pressure of the tin made the light almost entirely that of cadmium. It has since been stated that the gallium exerted its beneficial effects by virtue of its own impurities. Bismuth, lead or thallium are also effective, but should be limited to less than 1 per cent of the total filling.[76] The deterioration of the quartz envelopes of high-pressure lamps has been ascribed to attack by positive ions of the metal vapor, which have greater chemical activity than the atoms. This deterioration the Siemens-Halske Co.[77] propose to obviate by covering a part of the wall near the bulb or portion of the arc in which considerable potential drop occurs by an openwork metallic structure of spiral or braid or metal strips placed edgewise and not connected to a source of potential.[78]

A cadmium amalgam arc, especially intended as a source for the preparation of vitamin D,[79] is designed to avoid breakage on cooling by so arranging that on interruption of the discharge, the tube is automatically put in such a position that the free surface of the substance yielding the vapor is larger than when the lamp is in the working position. Carbon electrodes are used in a lamp employing a discharge in cadmium vapor mixed with nitrogen and hydrogen or a rare gas, and designed for television, the excitation of fluorescence, and for therapy.[80]

The Siemens and Halske Co.[81] proposed to stimulate the growth of plants by a lamp which emits predominantly in the region 3300 to 3600A. That such rays would prove effective was based upon the claims (by no means generally accepted) of workers with mitogenetic rays that dividing cells give out radiations of wave-length 3400A. This region was also claimed to be useful for healing purposes because of an alleged destructive action on virulent tumors. That sunlight lacks this property was claimed to be due to an antagonistic action of even low intensities of radiations in the wave-length region 3200 to 2900A. For the lamp, there was suggested an arc in quartz, one electrode being silver or zinc. The arc was to be drawn out as far as possible by a moving gas jacket. The intensity of the crater was to be reduced by fins or by water-cooling, the light from the center of the arc only being used. A filter for suppressing radiations of wave-lengths less than 3200A was also employed. Also an arc in vapors from alloys of the zinc group, such as zinc (17 per cent), cadmium (83 per cent) was proposed.[82]

Mitchell [83] compared three methods of securing the resonance lines of cadmium or zinc for use in physical studies of fluorescence. The methods utilized were the high potential discharge in a mixture of helium and zinc vapor,[84] a discharge tube

[74] Bates, F., *Bureau Standards Sci. Paper No. 371* (1920).

[75] Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **50**, 771 (1928).

[76] British P. 372,843, May 19, 1932, to Siemens and Halske, A.-G.

[77] British P. 397,680, August 31, 1933, to Siemens and Halske, A.-G.

[78] For details of the static characteristics of the high-pressure cadmium arc, see British P. 404,341, January 15, 1934, to Siemens and Halske, A.-G.

[79] British P. 366,366, February 4, 1932, to N. V. Philips' Gloeilampenfabriken. See also Elenbaas, W., and Jonas, G. B., U. S. P. 2,116,742, May 10, 1938; *Chem. Abs.*, **32**, 4891 (1938).

[80] British P. 418,128, October 18, 1934, to General Electric Co., Ltd., and Patent-Treuhand.

[81] British P. 296,724, February 24, 1930, to Siemens and Halske, A.-G. Silver-leaf filters transmitting between 3050 and 3300A, may be employed in the envelopes, according to C. J. Milner, British P. 485,787, May 25, 1938, to British Thomson-Houston Co.; *Chem. Abs.*, **32**, 7835 (1938).

[82] British P. 306,112, February 27, 1930, to Siemens & Halske Co.

[83] Mitchell, A. C. G., *J. Frank. Inst.*, **212**, 305 (1931).

[84] Ellett, A., *J. Opt. Soc. Am.*, **10**, 427 (1925).

of the Schüler type [85] with hollow cathodes, partly filled with zinc and an arc with hot equipotential, oxide-coated cathode; he found the latter to be the most economical and convenient. The arc was formed in a bulb filled with a helium discharge, and enclosed in a furnace with quartz windows, to vaporize a supply of zinc. The zinc lines began to appear at 330°C. At 370°C., the arc constricts and the helium is pumped out.

A xenon lamp has been described as a source of light in the extreme ultraviolet by Harteck and Oppenheimer.[86] The lamp is said to yield through a fluorite window the resonance lines of xenon at 1469 and 1295A. It can be operated for several hundred hours.

Manufacture of Quartz Products

Two scientific and engineering leaders had the foresight to grasp the industrial possibilities of the large-scale production of fused quartz, Prof. Elihu Thomson of the General Electric Co. at Lynn, Massachusetts, and Sir Richard Paget in England. Under their leadership, the experimental work developed independently in both countries. In England, the latter organized the Thermal Syndicate in 1903, which carried out early development under the direction of Hutton [87] and Dr. J. F. Bottomley. An account of the early work has been published by Paget.[88] The Syndicate early made opaque and translucent fused silica by fusion of glassmakers' sand. In 1906, the Silica Syndicate, Ltd., of London, worked patents of Kent and Lacell for the manufacture of transparent quartz glass. Other developments occurred in Germany, where Heraeus extended the work to the production of the tubes of mercury vapor lamps and Voelker founded a company in 1908, and in France where two companies, Le Quartz Fondu and Quartz et Silice have been producing since the war. The remarkable properties of this acid-resistant material, low solubility and low thermal expansion, made it of great importance to chemical and electrical industries and stimulated the large-scale development of the industry.[89]

The advances in America under the direction of Elihu Thomson in the Thomson Research Laboratory of the General Electric Co. at Lynn have been more closely concerned with the production of articles of clear or transparent quartz, for optical apparatus and for the transmission of ultraviolet radiations, the experimental work on which is largely due to Dr. E. R. Berry, P. K. Devers and L. B. Miller, although the opaque or coarser variety has also been developed by Mr. H. L. Watson. An account of the Lynn developments has been given by Dr. Thomson on the occasion of the presentation to him of the Franklin Medal of the Franklin Institute.[90] General reviews of the recent developments of the industry have been written by Moore [91] and Ibakh.[92]

[85] Schüler, H., *Z. Physik*, **35**, 323 (1926).

[86] Harteck, P., and Oppenheimer, F., *Z. physik. Chem.*, **16B**, 77 (1932); Groth, W., *Z. Elektrochem.*, **42**, 533 (1936).

[87] Hutton, R. S., *Trans. Am. Electrochem. Soc.*, **51**, 49 (1927).

[88] Paget, Sir R., *J. Roy. Soc. Arts*, April 4, 1924.

[89] Winship, W. W., *Trans. Am. Electrochem. Soc.*, **50**, 177 (1926).

[90] Thomson, E., *J. Frank. Inst.*, September, 1925.

[91] Moore, B., *Chemistry and Industry*, **50**, 671 (1931); *Trans. Ceram. Soc.*, **31**, 217 (1932); **32**, 45 (1933).

[92] Ibakh, B., *Keram. Steklo*, **8**, No. 8, 9 (1932) (Russian developments); *Chem. Abs.*, **27**, 821 (1933).

Chapter 9

Sources of Continuous Ultraviolet Radiations for Absorption Studies

In the measurement of ultraviolet absorption spectra, it is desirable that the source of illumination be continuous, or if that condition cannot be attained, the source should at least give a great number of closely spaced lines, so that there may be radiations of practically all wave-lengths available for absorption in the region studied. It is readily apparent that it would be futile to attempt to obtain the fine structure of an absorption band with the mercury arc as a source, since there are wide gaps in which no observations could be made.

One method of attaining this object would be to utilize as electrodes a number of metals, each of which emits many lines. The nature and amounts of the metals should be so chosen that gaps in the spectrum of one are filled by lines from the others. Such a source has been developed for the visible region.[1] The lines are not only closely spaced but are of very nearly equal intensity, so that the weaker ones can be photographed without overexposing the stronger ones. The electrodes are of carbon coated over with a fused mixture of the oxides of vanadium, titanium and molybdenum. The method is not, however, available as yet in the ultraviolet region. For measuring the broad fused systems of absorption bands of substances in condensed systems, that is, of liquids or of solutions, especially where a very high degree of quantitative accuracy is not required, the source of the ultraviolet radiations may be either the iron or the tungsten spark, both of which have many lines. Where it is desired to bring out the finer structure of the absorption bands, particularly in the case of gases, recourse is had to underwater sparks, to incandescent filament lamps burned at high voltage, to cathode-ray bombardment lamps, or to the hydrogen discharge tube.

Underwater Sparks. It has long been known that an arc can be made to burn and that sparks can be passed under liquids. In 1851, Masson [2] found the under-liquid arc to emit chiefly a continuous spectrum, although in the case of many metals, it has since been shown that there is superposed upon the continuous spectrum a bright-line spectrum. The underwater sparks from a large induction coil, between many metals, were studied by Wilsing,[3] who observed that some of the lines were reversed, that is, wholly dark, or bright but marked by a darkened center. The reversals are due to the absorption of emitted radiations by some of the metal vapor or by colloidal metal dispersed in the water. Being excited when dispersed, the atoms are in a condition to absorb many lines. The study of these reversals has been an aid in the classification of the lines of various metals.[4] Arcing or

[1] Eppley, M., *J. Frank. Inst.*, **201**, 233 (1926). Some of the new fluorescent lamps discussed in Chapter 8 may be of value as spectroscopic continuous sources for the visible and longer wave-lengths of the ultraviolet. Servigne, M., and Vassy, E., *Rev. optique*, **16**, 423 (1937); *Chem. Abs.*, **32**, 6154 (1938).

[2] Masson, M. A., *Ann. chim. phys.*, **31**, 295 (1851).

[3] Wilsing, J., *Astrophys. J.*, **10**, 113 (1899).

[4] Baly, E. C. C., "Spectroscopy," II, 128, London, Longmans, Green (1927).

sparking metals under liquids is one of the standard methods of dispersing the metals to form colloidal suspensions. Because of the turbidity thus produced, an arrangement for circulating the water must usually be provided when the underwater spark is employed as a source for absorption spectrophotography.

Among the first to employ the continuous spectrum emitted under water as a source for the study of the fine structure of absorption bands were Henri and de Laszlo.[5] Two condensers, each of 2.3×10^{-3} microfarad capacity, were connected in parallel and charged by a transformer supplied with a primary current of 20 amperes at 60 volts, interrupted 600 times a second. There was an auxiliary air spark gap of 15-20 millimeters and an underwater spark between rods of aluminum or copper. The spark was placed 5 centimeters below the surface and at a distance of 10-15 millimeters from a quartz window. The frequency of the oscillatory discharge was found to be of the order of one million per second. The spark was fairly uniform. An exposure of three to five minutes gave a continuous spectrum extending as far as 2100A.

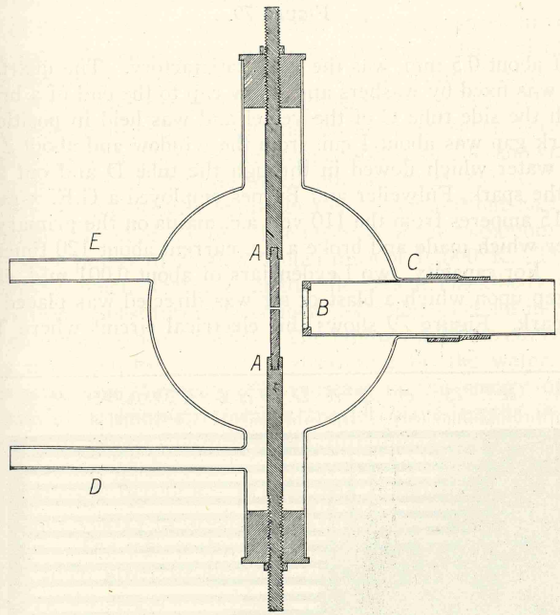


FIGURE 78.

Howe [6] and later Strachan [7] used brass electrodes, with 4 to 6 kw. in the primary of the transformer and secured a very satisfactory continuous spectrum extending to 2200A. Fulweiler and Barnes [8] omitted the Tesla coil and employed the arrangement shown in Figure 78.

[5] Henri, V., and de Laszlo, H. G., *Proc. Roy. Soc.*, **105A**, 668 (1924).

[6] Howe, H. E., *Phys. Rev.*, **8**, 674 (1916).

[7] Strachan, E. K., unpublished communication to Fulweiler, W. H., and Barnes, J., *J. Frank. Inst.*, **194**, 84 (1922).

[8] Fulweiler, W. H., and Barnes, J., *J. Frank. Inst.*, **194**, 83 (1922).

The electrodes A consisted of tungsten rods 3.5 mm. in diameter. These were mounted in brass rods which screwed into solid rubber stoppers. The stoppers were sealed with hard wax on the side tubes of a "Pyrex" glass bulb of about 500 cc. capacity. By means of the threads on the brass rods the position of the spark gap relative to the quartz window B, and also the length of the gap could be easily adjusted. Fulweiler and Barnes found under the electrical conditions used that a

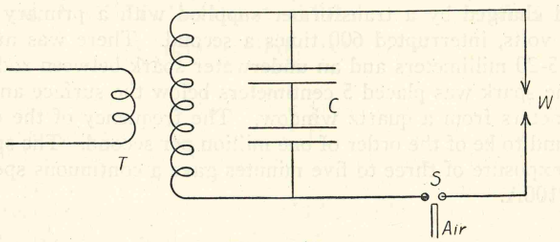


FIGURE 79.

spark length of about 0.5 mm. was the most satisfactory. The quartz plate B, 16.5 mm. diameter, was fixed by washers and screw cap to the end of a brass tube which slipped through the side tube C of the vessel and was held in position by a rubber tube. The spark gap was about 1 cm. from the window and about 2 cm. below the surface of the water which flowed in through the tube D and out at E. For the production of the spark, Fulweiler and Barnes employed a G.E. x-ray transformer, type K, using 15 amperes from the 110 volt a.c. mains on the primary coil. A mercury interrupter which made and broke a d.c. current about 120 times a second was also employed. For capacity, two Leyden jars of about 0.001 mfd. each were used. A zinc spark gap upon which a blast of air was directed was placed in series with the tungsten spark. Figure 79 shows this electrical circuit where T is the trans-

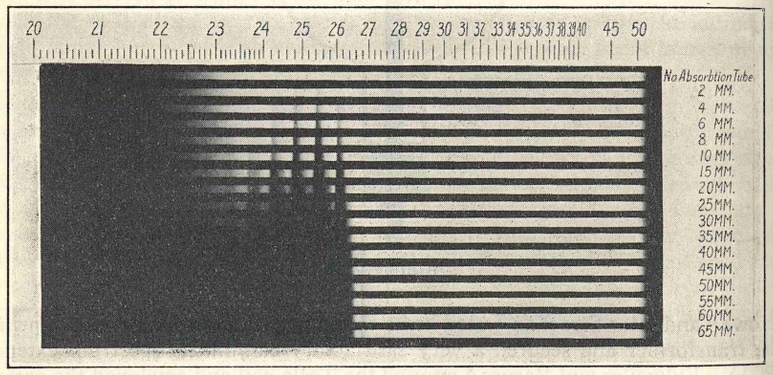


FIGURE 80.

former; C, the capacity; S, the external spark gap and W, the tungsten spark. The choice of tungsten for the electrodes was made after a careful trial of aluminum, brass, iron, nickel, carbon, tungsten and molybdenum. The tungsten gave more rays in the shorter wave-lengths and required very much less adjustment. Using 1.6

kilowatts in the primary of the transformer, the tungsten electrodes disintegrated very slowly compared with aluminum poles used under exactly the same conditions. Figure 80 illustrates the continuity of the spectrum thus obtained. The absorption bands are those of a 0.1-per cent solution of benzene in ethyl alcohol. The lengths of the solution used are indicated on the side of the plate. This photograph was taken with a Hilger quartz spectrograph. The top exposure with no absorption tube indicates the uniformity of the irradiation. In the original negative the spectrum extends to 2050A.

Snyder [9] employed a Tesla spark maintained under water, and utilized especially designed holders for the electrodes. Allin [10] found the uranium spark under water to give a perfectly continuous, intense spectrum with neither absorption nor emission lines. McNicholas [11] employs spark terminals of tungsten (with about a 16 millimeter gap) enclosed in an ebonite box through which a stream of distilled water is circulated. The adjustment and centering of the spark is accomplished by external controls. Lewis [12] has compared ductile uranium, tungsten-steel and aluminum as electrode materials for the underwater spark.[13]

The theory of the continuous nature of the underwater spark in relation to black body radiation has awakened some interest. Wilson [14] has calculated from the position of the intensity maximum of the OH absorption bands in some spark spectra that the effective temperature of the underwater spark is 5115°. Wyneken [15] determined the energy distribution of the underwater spark between aluminum electrodes by photographic-photometric comparison with the known energy distribution of the carbon arc. A definite maximum occurs at 2850A, (with aluminum electrodes) where the intensity is approximately three and one-half times as great as it is in the neighborhood of 4500A. The position of the maximum would indicate, if the radiation were purely thermal, a temperature of 10,000°K. The experimental curve was, however, much steeper than the theoretical black-body radiation curve for this temperature. Substitution of copper electrodes gave no indication that the curve depends on the electrode material. The falling off of the curve in the extreme ultraviolet was not regarded as due to absorption by the water. Very similar results were reported by Wrede.[16] An increase in the energy of the discharge displaces the maximum intensity towards shorter wave-lengths in conformity, in the case of zinc, with Wien's law for temperature radiation. For smaller discharge energy, the temperature of the spark was calculated to be of the order of 7500°K. and for greater energy 10,000°K. In the case of aluminum and magnesium the shift with increasing energy of discharge was less marked than with zinc, cadmium, copper, lead or tin. The temperatures so determined refer to the inner part of the spark, while the much lower temperature found by Wilson probably refers to the mantle surrounding the spark, since his determination was made by calculation from the maximum absorption of a band spectrum. By this method, Stücklen [17] calculated the temperature of the absorbing OH mantle around the underwater copper spark to be 3000°Abs.

[9] Snyder, V. D., *J. Am. Chem. Soc.*, **49**, 2510 (1927).
[10] Allin, E. J., *Trans. Roy. Soc. Canada*, **21**, Section 3, 231 (1927).
[11] McNicholas, H. J., *Bureau Standards J. Research*, **1**, 939 (1928). Details of construction also are given.
[12] Lewis, S. J., *Chemistry and Industry*, 464, **1933**.
[13] See also Tyndall, E. P. T., *Bureau Standards Tech. Paper, 148* (1920), appendix.
[14] Wilson, E. D., *J. Opt. Soc. Am.*, **17**, 37 (1928).
[15] Wyneken, I., *Ann. Physik*, **86**, 1071 (1928)
[16] Wrede, B., *Ann. Physik*, **3**, 823 (1929).
[17] Stücklen, H., *Naturwiss.*, **18**, 248 (1930).

Incandescent Sources. Cohn and Andresen-Kraft [18] suggested as a continuous source for absorption work, the light from cathode-ray bombardment (either in a gas or high vacuum) of a thorium-layered anode. The spectrum was said to extend from 2200 to 6000A, with a maximum intensity at 4500A. Weingeroff,[19] however, did not believe this source to meet the requirements of a truly continuous spectrum. De Kowalski [20] and later Gelhoff [21] used tungsten lamps at 20 to 30 per cent over-rating. (See Chapter 3.) This method gives a continuous but somewhat expensive source, as the lamps burn out quickly. In lamps intended for such use,[22] the filament may be put half as close as usual to the wall, a portion of the latter being of quartz. Weingeroff described a source in which a tungsten cylinder in vacuum, nitrogen or a noble gas is made to glow by an electric current. The Osram Co. produce a tungsten lamp in Uviol glass which operates at 250 volts and 2 amperes, and transmits a continuous spectrum to 2900A.

Hydrogen Discharge Tube. The continuous molecular hydrogen spectrum was first observed by Dove,[23] according to Chalonge and Zé.[24] Freeman has traced the history of work on this phenomenon.[25] It was shown by Horton and Davies [26] that slow-moving electrons in hydrogen produce a continuous spectrum. Lemon,[27] using a discharge tube with a Wehnelt cathode, found that by varying the filament temperature, he could get in succession, and almost pure, Balmer lines, the molecular spectrum of hydrogen and the continuous spectrum.[28] Carst [29] concluded, as did Horton and Davies, that the hydrogen molecule is the carrier of the spectrum, which is distinct from the continuous spectrum which is to be expected at the series limit. The use of the hydrogen discharge tube as a source of continuous ultraviolet radiation was introduced by Tingey and Gerke.[30] Their source, however, lacked intensity, and exposures of at least an hour often were necessary.

Gehrcke and Lau [31] described the structureless nature of radiations emitted between 3300 and 1950A by pure hydrogen in an alternating current discharge in an inside silvered tube. Bonhoeffer and Steiner [32] employed this source in the absorption spectrophotometry of hydrogen iodide.

A great impetus to the more general use of the hydrogen discharge came from the work of Bay and Steiner,[33] who increased the intensity by employing an end-on arrangement. Also the current density was made as high as possible by loading the tube heavily. They employed aluminum electrodes extending close to the walls, the electrodes having areas of 300 square centimeters. It was stated that the electrodes could carry as much as 500 milliamperes for a day. To get the current

[18] Cohn, W. M., and Andresen-Kraft, C., *Z. tech. Physik,* **12,** 428 (1931); *J. Am. Ceram. Soc.,* **15,** 122 (1933).
[19] Weingeroff, M. A., *Physik. Z. Sowj.,* **2,** 278 (1932).
[20] de Kowalski, J., *Arch. des Sciences,* **37,** 265 (1914).
[21] Gelhoff, G., *Z. tech. Physik,* **1,** 224 (1920).
[22] British P. 359,712, October 29, 1931, to N. V. Philips' Gloeilampenfabrieken.
[23] Dove, *Pogg. Ann.,* **104,** 186 (1858).
[24] Chalonge, D., and Zé, N. T., *J. Phys. Radium (7),* **1,** 416 (1930).
[25] Freeman, I. M., *Astrophys. J.,* **64,** 122 (1926).
[26] Horton, F., and Davies, A. C., *Phil. Mag.,* **46,** 892 (1923).
[27] Lemon, H. B., *Nature,* **113,** 127 (1924).
[28] See also Richardson, O. W., and Tanaka, T., *Proc. Roy. Soc.,* **106A,** 640 (1924).
[29] Carst, A., *Ann. Physik,* **75,** 665 (1924).
[30] Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.,* **48,** 1838 (1926); see also Bates, J. R., and Taylor, H. S., *Ibid.,* **49,** 2441 (1927).
[31] Gehrcke, E., and Lau, E., *Ann. Physik,* **76,** 673 (1925).
[32] Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.,* **122,** 287 (1926).
[33] Bay, Z., and Steiner, W., *Z. Physik,* **45,** 337 (1927).

density high, the luminous portion of the tube was constricted. One of their tubes was water-cooled at the constriction. The tube (Figure 81) consisted of an ordinary glass tube (L) 60 centimeters long and 5 millimeters in diameter X, two electrode vessels (G), one of which has a tube (R) carrying a quartz or fluorite window and the other a 5-liter bulb (V). The apparatus was supported with the lower luminous tube in a bath with flowing water. The tube was filled with hydrogen at 1-2 millimeters pressure and sealed. Failures of these tubes led them to develop a tube that would operate under loads up to 500 or even 700 milliamperes,[34] which is important since the ultraviolet emission increases with the current density. The ratio of ultraviolet emission to the radiations in the visible range increases with the hydrogen pressure. For the continuous radiation from the hydrogen lamp, the ratio is 6:1, while that of the mercury lamp is only 0.6:1. Bay and Steiner [35] also made use of an electrodeless oscillating discharge in well-dried hydrogen.

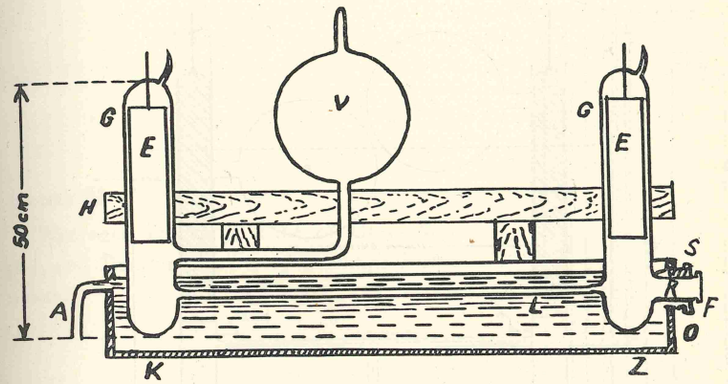


FIGURE 81. Hydrogen Discharge Tube of Bay and Steiner *(Zeitschrift für Physik).*

Another development of the discharge tube was made by Lambrey and Chalonge,[36] who used only 15-30 milliamperes to operate the tube for five minutes. They [37] extended their work to include tubes with both interior electrodes and tubes with only exterior electrodes operating at 500,000 cycles. They found that as the pressure increases, the intensity of the continuous spectrum passes through a maximum at a hydrogen pressure of 2-3 mm. For a given pressure, the intensity increases with the current, but the energy distribution is not modified. As compared with a carbon arc, the intensity is about 2.1 times as great at 4400A and 23 times as great at 2200A.[38]

Considerably greater currents were carried in a tube devised by Lawrence and Edlefsen.[39] The electrodes were aluminum cylinders 6 centimeters in diameter and 40 centimeters long, open at the bottom and closed at the top, and attached to tungsten leads passing through "Pyrex" containing tubes. The bottom edges of elec-

[34] Bay, Z., and Steiner, W., *Z. Physik,* **59,** 48 (1929).
[35] Bay, Z., and Steiner, W., *Z. Elektrochem.,* **34,** 657 (1928).
[36] Lambrey, M., and Chalonge, D., *Compt. rend.,* **184,** 1057 (1927).
[37] Lambrey, M., and Chalonge, D., *Compt. rend.,* **188,** 1104 (1929).
[38] See also Chalonge, D., and Zé, N. T., *Compt. rend.,* **190,** 632 (1930); Chalonge, D., *Z. Astrophys.,* **15,** 82 (1938).
[39] Lawrence, E. O., and Edlefsen, N. E., *Rev. Sci. Instruments,* **1,** 45 (1930).

trodes were rounded off and made close-fitting to the containing tubes for cooling by conduction. The two large "Pyrex" tubes containing the electrodes were joined through a tube of quartz 7 millimeters in diameter and 60 centimeters long. The connecting tube was sealed to the confining tubes by a water-cooled wax joint. The tube was insealed into short quartz tubes of larger diameter at each end and the larger quartz tubes were waxed to "Pyrex" side tubes. Two inflow jets of water flowed in the region between the small and large quartz tubes and kept the wax joints cool despite the great generation of heat nearby. The whole tube was immersed in a tank of water to the dotted line (Figure 82). This cooling was adequate for 6.5 amperes at 3000 volts, but the tube was ordinarily run at 3 amperes. There was some unsteadiness and bumping at the middle of the connecting tube unless additional water jets were provided along the quartz tube. The tube was used end-on, through a quartz window W waxed on a "Pyrex" side tube through the tank wall.

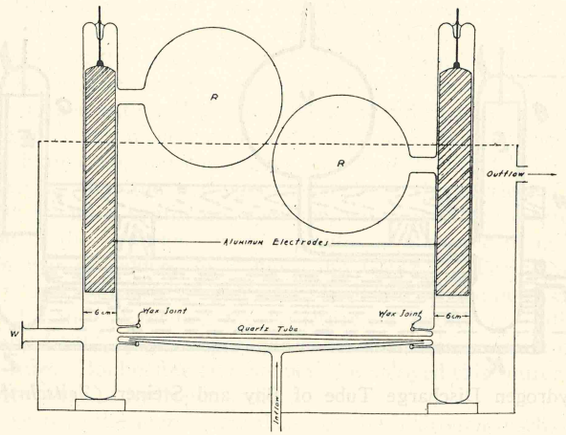


FIGURE 82. Water-cooled Hydrogen Discharge Tube of Great Carrying Capacity (Lawrence and Edlefson, *Review of Scientific Instruments*).

It was only necessary to evacuate the tube by an oil pump to 0.01 millimeter and flush it several times with commercial tank hydrogen. The pressure was not very critical, and the hydrogen pressure was merely reduced to allow a discharge of several amperes to pass at 3000 volts. Lines appeared at first but after several hours to a day of operation, the lines due to impurities disappeared and the region from 3000 to 2000A became continuous. Two large flasks (R) served as hydrogen reservoirs. The tube could be operated steadily over long periods. Data obtained by the aid of a monochromator and thermopile indicated that the intensity of the ultraviolet does not vary greatly from the near ultraviolet to 2000A. The intensity at 2536A seemed of the same order as that obtained from a Cooper-Hewitt lamp at ordinary currents. The tube yielded about ten times the intensity of the first Bay and Steiner tubes, and was much more intense than the usual ultraviolet available for spectroscopy, exposures of 0.1 second being adequate.

Other tubes were described by Kistiakowsky[40] and by Urey, Murphy and

[40] Kistiakowsky, G. B., *Rev. Sci. Instruments*, 2, 549 (1931).

Duncan.[41] The latter tube, of glass, was very compact and so well cooled that currents up to 2 amperes could be carried for long exposures without breakage. One end only is indicated in Figure 83; the other is identical. The tube was composed of "Pyrex" with crystal quartz windows stuck on each end with de Khotinsky cement. The electrodes D were cylinders of sheet aluminum, the edges of which were spot welded. They were joined to the tungsten lead A by German silver wire. The electrodes were held by glass prongs. A rapid stream of water flowed into B and after circulating around the inner tube flowed out again at the other end. Two small cooling jackets were placed near the windows to prevent the wax from getting warm, but they did not seem necessary. The inner tube through which the discharge passed was moistened with silver nitrate solution which was readily

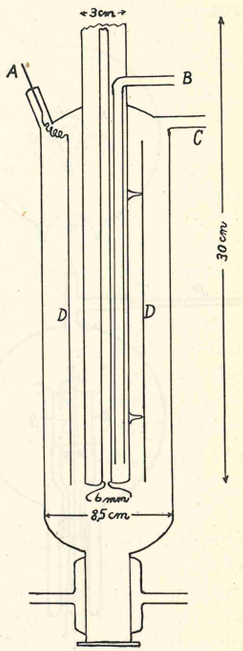


FIGURE 83.

Hydrogen Discharge Tube of Urey, Murphy, and Duncan *(Review of Scientific Instruments)*.

reduced to silver by the discharge. The tube was evacuated at C and in the same position at the other end a palladium tube was connected by a soft glass-to-"Pyrex" graded seal. Hydrogen was admitted through the palladium by heating the latter with a small hydrogen flame. The discharge was run repeatedly with the addition of hydrogen and evacuation until the spectrum seemed satisfactory, as viewed with a direct-vision spectroscope. The tube was sealed off from the pumping system at C. As the hydrogen gradually cleaned up, more could easily be added at the palladium tube. A 5-kv. autoregulating transformer supplied the high potential. With 110 volts and about 50 amperes on the primary, it gave 2500 volts on the secondary. An ammeter in series with the tube showed 2 amperes under the best operating conditions. A fan was directed on the outside of the tube as a further aid to

[41] Urey, H. C., Murphy, G. M., and Duncan, J. A., *Rev. Sci. Instruments*, 3, 497 (1932)

cooling. Even after long exposures, the tube remained quite cool, and was satisfactory after a year of use. Employed with the Hilger E1 spectrograph, it was possible to obtain certain bands of nitric oxide at 2050 and 2150A in absorption with exposures of one to five minutes, using Eastman U. V. Spectroscopic Plates. Dawson [42] described a tube for discharge in hydrogen at 30 to 100 millimeters pressure. The tube could be viewed side-on through a constricted quartz tube joining two hollow electrodes in glass supporting tubes.[43]

According to Henry, the hydrogen discharge tube has become the most suitable and probably also the most used continuous source.[44] Most such tubes give intensities which are too weak. Henry modified somewhat the disposition of the electrodes and employed hydrogen at a pressure of 4 millimeters. He used 1200 volts at the electrodes and usually 2 amperes, although this could be raised to 3.5 to 4 amperes.

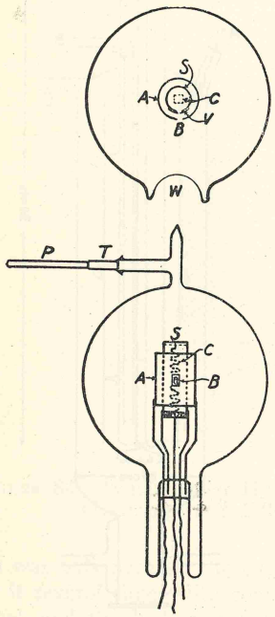


FIGURE 84.

Hydrogen Discharge Tube of Munch *(Journal American Chemical Society).*

Munch [45] states that the hydrogen continuum may be excited at about 5 per cent of the voltage required by other discharge tubes and without water cooling, by means of thermoelectrons from a hot cathode. For example, the low voltage arc of Duffendack and Manley [46] may be utilized. This arc passed between a heated tungsten filament and a disk anode, in a tube containing a palladium tube to admit hydrogen and a quartz window sealed on with wax. Munch modified this tube by employing an oxide-coated cathode (C in Figure 84). This cathode is a 0.48 × 15.25 centimeter piece of nickel gauze bent into a corrugated form having a 0.48 centimeter cross-

[42] Dawson, L. H., U. S. P. 1,922,281, Aug. 15, 1933; *Chem. Abs.*, **27**, 5006 (1933).
[43] See also Stevens, D. S., *Rev. Sci. Instruments*, **6**, 40 (1935).
[44] Henry, L., *J. chim. phys.*, **31**, 665 (1934).
[45] Munch, R. H., *J. Am. Chem. Soc.*, **57**, 1863 (1935).
[46] Duffendack, O. S., and Manley, J. H., *J. Opt. Soc. Am.*, **24**, 222 (1934).

section, suspended between a cathode shield of nickel and a nickel wire and coated with barium and strontium carbonates. The cylindrical cathode shield, S, of 0.125 millimeter nickel, 4.06 centimeters long and 1.25 centimeters in diameter, forms one lead to the cathode and is closed at the bottom by means of a porcelain disk through which the second cathode lead passes. The only opening in the shield is a 0.66 × 3 millimeter slit cut in a piece of 0.25 millimeter sheet tungsten welded in the side. The surrounding anode (A) is a 2.2 × 2.86 centimeter nickel cylinder with a hole (B) to correspond to the slit in the cathode shield. The electrodes are mounted on a five-wire stem and sealed into a 10-centimeter "Pyrex" bulb. A thin window (W) is made opposite the slits by blowing a bubble about 3.2 centimeters in diameter, melting it back to about half its height and sucking it in carefully. The palladium tube (P) is silver soldered to a copper tube (T) the end of which is flared and sealed on the outside of a piece of Nonex which is fused to the "Pyrex" from which the bulb is made. The tube is evacuated and freed of all traces of moisture or carbon monoxide. The glass and metal parts are outgassed by passing a discharge through the tube and sweeping it out with a stream of hydrogen at 2-4 millimeters pressure. The hydrogen is admitted by holding a Bunsen burner under the palladium tube. When the spectrum becomes continuous below 3657A, the tube is sealed off. The cathode requires 9 amperes at about 3 volts, supplied by a step-down transformer and connected in series with a rheostat and ammeter. The anode circuit, also containing a rheostat and ammeter, may be connected to any 110-volt circuit. In operation, the potential drop between anode and cathode is 30-35 volts. The whole discharge between the cathode and anode must pass through the small slit in the shield and is viewed through the opening in the anode. It can operate continuously at a current of 1.5 ampere, the current density being 75 amperes per square centimeter. This may be increased considerably for short periods. In comparison with the intensity of the mercury lines of a "Labarc," both sources being run at 1 ampere, the continuum was 25 per cent as intense as the 2483 and 2652A lines, 7 per cent as intense as the 2894 and 3022A lines and 12 per cent as intense as the 3350A lines.

Other descriptions of tubes for this purpose were made by Watson and Hurst,[47] Almasy and Kortüm,[48] Jacoby,[49] and Smith.[50] Hydrogen discharge tubes carrying up to 1 ampere have been prepared by the Hanovia Co.

According to the Hilger Co., the distribution of radiation from hydrogen discharge tubes is so far from uniform that the tubes cannot be used for measurements of density with their "Spekker" photometer. Furthermore, when run on alternating current, the intensity of radiation increases to a maximum and dies away to zero once in each half-phase of the applied alternating current, so that it cannot be assumed that for any speed at which the use of a sector fulfills the reciprocity law, the effective density of the sector can be derived from its aperture. To overcome this, a rocking quartz tube has been made available. Its speed of oscillation is such that the energy received by the apertures of the "Spekker" photometer is uniform over that area, in a vertical plane, for all exposures over twenty seconds.

Smith and Fowler [51] have described a 220-volt d.c. discharge tube which can be operated with currents as high as 20 amperes to give an intense ultraviolet continuum. (Figure 85). The cathode of 25 cm. of 40 mil tungsten wire was attached

[47] Watson, W. H., and Hurst, D. G., *Can. J. Research*, **13A**, 19 (1935).
[48] Almasy, F., and Kortüm, G., *Z. Elektrochem.*, **42**, 607 (1936).
[49] Jacoby, G., *Z. tech. Physik*, **17**, 382 (1936); *Physik. Z.* **37**, 808 (1936).
[50] Smith, N. D., *J. Opt. Soc. Am.*, **32**, 2832 (1938). This tube uses a 5.3 cm. capillary of rectangular cross-section 1.3 × 6 mm., with a gas pressure of 1-2 mm.
[51] Smith, A. E., and Fowler, R. D., *J. Opt. Soc. Am.*, **26**, 79 (1936).

to the water-cooled cathode leads of copper tubing by set screws. The leads were attached to the "Pyrex" cathode section (C) by copper-to-"Pyrex" seals (F). The filament current (50-60 amperes) was supplied by a 220 to 30-volt transformer. The discharge tube (A) was of 7 mm. inside diameter quartz tubing attached to a 100 cc. quartz flask, which was sealed with picein to a water-cooled metal ring (B). This metal ring in turn was sealed with picein to the cathode section (C). The anode consisted of a hollow copper male joint (D), sealed with picein to a No. 50 Pyrex joint (E), the anode chamber. The latter was attached to the quartz discharge tube by means of a water-cooled picein seal. A quartz window was sealed to

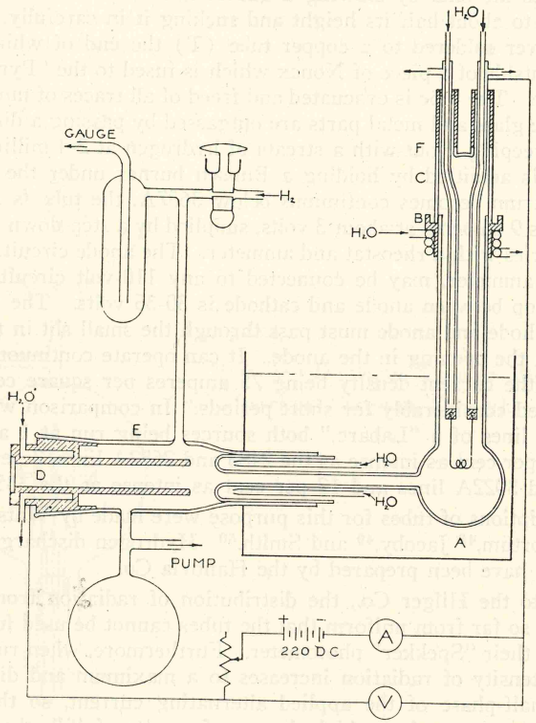


FIGURE 85. Hydrogen Discharge Tube of Smith and Fowler *(Journal Optical Society of America)*.

the far end of the hollow anode. For a given potential across the tube, the pressure for greatest intensity of the continuum was not very critical, but it varied greatly with the voltage. Pressures of 0.20 to 0.27 mm. were usually employed with potentials of 220 volts.

THEORY OF THE CONTINUOUS SPECTRA OF HYDROGEN

To discuss the many investigations directed toward an understanding of the theory of the origin of the continuous spectrum which extends from the visible to the Schumann region would lead us far beyond the scope of this book. A thorough discussion of the origin of the continuous spectra of gases, with 323 references, has

been given by Finkelnburg.[52] Chalonge and Zé [53] have reviewed in detail the work relating to the hydrogen spectrum. Beyond the Balmer lines there lies (as discussed in Chapter 2) a continuous spectrum related to the excitation of the hydrogen atom beyond its ionization potential, as explained by Bohr.[54] In the discharge tube, the Balmer lines are widened by the Stark effect and the related continuous spectrum is displaced toward the red. Chalonge and Zé [55] have found evidence also for the existence of another continuous spectrum similarly related to the Paschen series of lines and extending into the infrared.

These continuous spectra are not, however, very significant in the radiations emitted by the tubes described in the preceding section. The effective continuous spectrum is related to the hydrogen molecule, which itself produces a "secondary," many-lined, or band, spectrum, regarding which there is a vast literature. One of the earliest theories relating the hydrogen molecule to the continuous spectrum produced in these sources assumed the spectrum to be due to dissociation of the hydrogen molecules into atoms possessing various kinetic energies, the radiations being emitted during their recombination.[56]

Discrepancies in regard to the relation between the heat of dissociation of the hydrogen molecule and the long wave-length limit of the continuum led to a number of suggestions in which variously excited, rather than resting state, molecules were regarded as dissociating.[57]

More recently, efforts have been directed toward the examination of the potential energy curves for the atoms of the hydrogen molecule from the standpoint of the wave-mechanics, the general features of which in relation to photochemistry are discussed in Chapter 13. For the reader desiring to study the application of these theoretical developments to the hydrogen continuum a few significant papers are cited.[58]

[52] Finkelnburg, W., *Physik. Z.*, **31**, 1 (1930).

[53] Chalonge, D., and Zé, N. T., *J. Phys. Radium*, (7) **1**, 416 (1930).

[54] Bohr, N., *Phil. Mag.*, **26**, 17 (1913).

[55] Chalonge, D., and Zé, N. T., *Compt. rend.*, **189**, 243 (1929); **190**, 425 (1930).

[56] Schüler, H., and Wolf, K. L., *Z. Physik*, **33**, 42 (1925).

[57] Takahashi, Y., *Japan. J. Phys.*, **4**, 103 (1927); *Chem. Abs.*, **21**, 3829 (1927). Takahashi, Y. and Fukumoto, Y., *Sci. Repts. Tohôku Imp. Univ.*, **17**, 675, 963 (1928); *Chem. Abs.*, **23**, 3834 (1929). Freeman, I., *Astrophys. J.*, **64**, 122 (1926). Oldenberg, O., *Z. Physik*, **41**, 1 (1927). Herzberg, G., *Physik. Z.*, **28**, 727 (1927). Jezewski, H., *Compt. rend. soc. polonaise phys.*, **3**, 161 (1927); *Chem. Abs.*, **23**, 5106 (1929). Newman, *Phil. Mag.*, **6**, 807 (1928). Kaplan, J., *Proc. Nat. Acad. Sci.*, **13**, 760 (1927). Winans, J. G., and Stueckelberg, E. C. G., *Ibid.*, **14**, 867 (1928); Franck, J., and Jordan, P., "Anregung von Quantensprungen durch Stösse," p. 261, Berlin, J. Springer, **1927**.

[58] Heitler, W., and London, F., *Z. Physik*, **44**, 455 (1927). Sugiura, Y., *Z. Physik*, **45**, 484 (1927); *J. Phys. Radium*, **8**, 113 (1927). Birge, R., *Proc. Nat. Acad. Sci.*, **13**, 462 (1927). Condon, E. U., *Phys. Rev.*, **28**, 1182 (1926); *Proc. Nat. Acad. Sci.*, **13**, 462 (1927). Franck, J., *Trans. Faraday Soc.*, **21**, part 3, (1925). Epstein, P. S., and Muskat, M., *Proc. Nat. Acad. Sci.*, **15**, 405 (1929). Goldstein, L., *Compt. rend.*, **193**, 485 (1931). Smith, A. E. and Fowler, R. D., *J. Opt. Soc. Am.*, **26**, 79 (1936); McDonald, J. K. L., *Proc. Roy. Soc.*, **A 136**, 528 (1932). Finkelnburg, W., and Weizel, W., *Z. Physik*, **68**, 577 (1931).

Chapter 10

Protective Glasses, Ultraviolet-Transmitting Glasses and Filters

The ability of glasses of various compositions to absorb or transmit ultraviolet or other radiations is of importance when viewed from either of two opposite aspects. It may be desired on the one hand to develop a glass capable of protecting the eyes of a worker from injurious radiations, or, on the other, it may be desired to produce a glass which transmits the solar ultraviolet more completely than ordinary window glass.[1] Mention of protective glasses is made here to remind the experimentalist not to disregard suitable protection for the eyes when working with ultraviolet rays.

Protective Glasses

Exposure to rays emitted in electric welding and in the employment of the oxy-acetylene torch for cutting and welding steel has been the cause of many cases of inflammation of the eyes. In arc welding, the eyes require protection from intense visible light or glare, from intense infrared or heat rays and from ultraviolet radiations. Andrews [2] affirms that the ultraviolet rays are the most dangerous because they are not only invisible but also because we are unprovided by nature with any organ or sense for detecting them. Furthermore, it should be noted that the harmful effects are not immediately produced but become evident only some time after the exposure. Fortunately, the most deleterious of the ultraviolet rays are absorbed by a moderate thickness of ordinary glass.

The symptoms of conjunctivitis caused by intense light or by ultraviolet rays are abnormal intolerance to light, excessive secretion of tears, intense smarting of the lids, contraction of the pupils, sometimes swelling of the lids, and more rarely, small ulcers developing on the eyeball or cornea. Fortunately, the lesions are usually superficial, because the cornea absorbs all radiations below 3000A and the lens those below 3500A, thereby protecting the retina. However, unless properly treated by a physician, infection may occur, resulting in chronic inflammation of the conjunctiva, cornea, iris or retina and possibly blindness. Under proper treatment, most cases recover in a few days.

In 1914, Crookes [3] investigated over 300 specimens of glass in an endeavor to find a colorless glass which would absorb all the ultraviolet and infrared rays. Although he did not find a colorless glass which met this specification, he developed a blue-green glass which absorbed about 90 per cent of the radiant heat and which was opaque to ultraviolet rays. The glass was sufficiently free from color to be scarcely noticeable when used as spectacles. The ideal glass which will transmit all

[1] Chance, W. H. S., and Hampton, W. M., [*Proc. Optical Convention,* **1926,** I, 24; *Chem. Abs.,* **21,** 3111 (1927)], reviewed the early manufacture of the filtering glasses produced by Chance Bros. & Co., Ltd. Methods of measuring the transmission of ultraviolet rays by glasses were discussed by Shapiro, C. V., *Am. J. Physiol.,* **87,** 396 (1928), and Schachtschabel, K., *Ann. Physik,* **81,** 929 (1926).

[2] Andrews, W. S., *Gen. Electric Rev.,* **9,** 303 (1917).

[3] Crookes, W., *Trans. Roy. Socz.,* **214,** 1 (1914).

the colors of the spectrum, cutting off the invisible rays at each end, has still to be discovered.

Luckiesh,[4] Gage [5] and Martin [6] have given data on the transmission of the earlier commercial protective glasses. The latter also have been studied at the Bureau of Standards.[7]

A number of commercial glasses, including 82 examined by Gibson and McNicholas, were investigated. Crookes A, Corning 91B, American Optical Co. Nos. 57 and 58, and Noviol O were most efficient in protecting against ultraviolet rays. The latter two, the most efficient, were not nearly so colorless as the other three. A combination of Noviol A and Corning 124J absorbs all the ultraviolet and most of the infrared and, although light green, still has a high visible transmission.[8] The Bureau developed a blue glass for furnace workers by replacing half the lime in a soft soda-lime glass with cerium oxide to stop the ultraviolet and adding sufficient cobalt oxide to produce the blue color desired by workmen. The glass registered 20 + 8 on the Lovibond scale.[9] The glass may contain SiO_2 60-80, CaO 0-12, CeO 5-10, CoO 0.1-0.5 and Na_2O 12-25 percent.[10] A thin film of gold [11] absorbs infrared and ultraviolet and to some extent visible rays, depending upon the density of the film.[12] Inagaki reported Noviweld and certain Crookes glasses suitable for specified uses in glass plants.[13] Coblentz and Stair [14] have published transmission curves of optical crown glass, and several commercial protective glasses. See Figure 86.[14a] Average samples of colorless, vitreous silica were much more opaque than was quartz to radiation shorter than 2400A. A formula for specifying the shade number of protective glasses, based upon experimental tests, was given, together with a table of transmissions and tolerances, corresponding to shade numbers, as proposed by a Federal specification committee. The specifications were somewhat revised in 1930.[15]

A glass advocated by the Corning Glass Works [16] for absorbing ultraviolet radiations is made by adding to an ordinary lime, barium, lead, or zinc glass batch; (A) at least 6 per cent of titanium dioxide, and oxidizing salt (nitre) in sufficient quantity to prevent the reduction of the titanium dioxide, with or without cerium oxide or vanadium oxide; or (B) at least 1 per cent of an oxide of vanadium higher

[4] Luckiesh, M., *Trans. Ill. Eng. Soc.,* **9,** 472 (1914).

[5] Gage, H. P., *Ibid.,* **11,** 1050 (1916); **25,** 337 (1930).

[6] Martin, L. C., *Trans. Opt. Soc.,* **18,** April (1917).

[7] Coblentz, W. W., and Emerson, W. B., Tech. Paper No. 93 (1917), *Bureau of Standards; J. Frank. Inst.,* **183,** 629 (1917); Coblentz, W. W., Emerson, W. B., and Long, M. B., *Bull. Bureau of Standards,* **14,** 663 (1918); *J. Frank. Inst.,* **188,** 255 (1919); Gibson, K. S., and McNicholas, H. J., *Bureau of Standards Tech. Paper No. 119* (1919); *J. Frank. Inst.,* **187,** 630 (1919). For data on the absorption of cobalt glasses, see Brode, W., *J. Am. Chem. Soc.,* **55,** 939 (1933).

[8] See also Wright, P., *Brit. J. Radiology,* **2,** 434 (1929).

[9] *Ind. Eng. Chem., News Ed.,* **3,** No. 24, 6 (1925); Coblentz, W. W., U. S. P. 1,637,439, Aug. 2, 1927; *Chem. Abs.,* **21,** 3114 (1927).

[10] Coblentz, W. W., and Finn, A., *J. Am. Ceram. Soc.,* **9,** 423 (1926); *Brit. Chem. Abs.,* **B,** 667 (1926).

[11] Finely divided gold particles have also been proposed; Warde, F. M., British P. 341,187, Nov. 15, 1929; *Chem. Abs.,* **27,** 2272 (1933).

[12] See Grondall, L. O., *Science,* **70,** 179 (1929). For other metallic films obtained by cathodic sputtering, see Taylor, E. M., Stafford, G., and Rodwell, R. V., and Kapella, Ltd., British P. 479,238, Feb. 2, 1938; *Chem. Abs.,* **32,** 4938 (1938).

[13] Inagaki, T., *Rept. Lab. Asahi Glass Co.,* 1921; *Chem. Abs.,* **16,** 3185 (1922).

[14] Coblentz, W. W., and Stair, R., *U. S. Bureau Standards Tech. Paper* No. 369, 555 (1928).

[14a] The transmissions of several miscellaneous materials, as mother-of-pearl, sextant and signal glasses, heat-transmitting glass, greenish-brown glass, and the organic materials "pollopas" and "protectoid" were also given.

[15] Coblentz, W. W., and Stair, R., *J. Opt. Soc. Am.,* **20,** 624 (1930).

[16] British P. 118,397 and 118,398, April 15, 1918, to Corning Glass Works; *J. Soc. Chem. Ind.,* 584A, 1918. For snow glasses, see also Degea, A.-G., British P. 466,262, May 25, 1937; *Chem. Abs.,* **31,** 8144 (1937).

than V_2O_3, with or without an oxidizing agent and a complementary, but absorptively inert substance (manganese dioxide, cobalt, nickel or uranium oxide) to change the hue of the glass from green to amber. Titanium dioxide is about half as effective as cerium oxide. A lime-soda glass containing 7.7 per cent titanium dioxide and 7.7 per cent cerium nitrate is a brilliant clear yellow, and in plates two mm. thick completely cuts off the 3650A line. A glass containing both cerium nitrate and titanium dioxide has a more brilliant color and greater desirable absorption than a glass containing one of these substances superimposed on a glass containing the other. The addition of borax increases the refractive index of the glasses containing titanium dioxide. A large percentage of borax in a glass containing

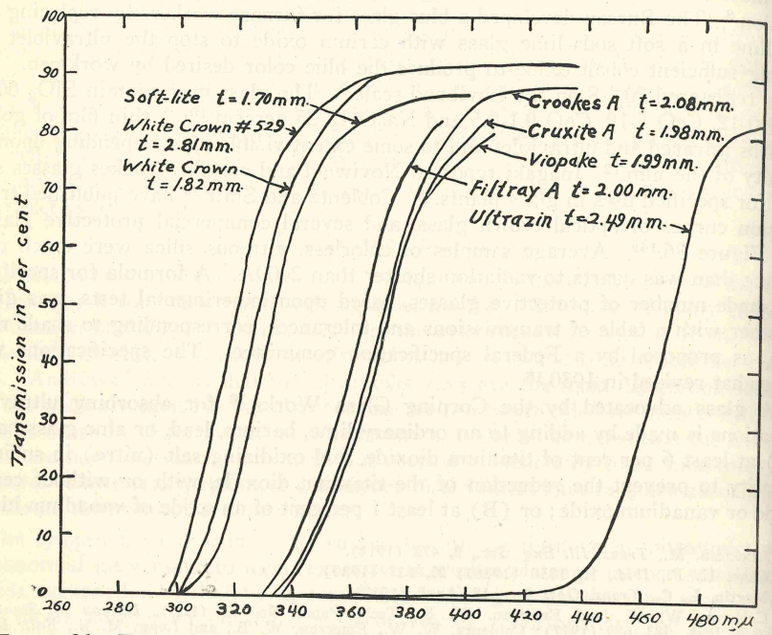


FIGURE 86. Transmission Curves for Various Protective Glasses (Coblentz and Stair, "Bureau of Standards Technical Papers").

vanadium oxide completely cuts off the ultraviolet 3650A line in plates of 4 mm. thickness. If 2 per cent of vanadium oxide be used, the same cut-off is effected by plates 2 mm. thick.

Up to 10 per cent of rare earths is used by Deutsche Spiegelglas A.-G.[17] Taylor[18] describes a glass for absorbing ultraviolet rays in which titanium oxide is an essential constitutent. He also[19] obtains a flesh-colored glass of high ultraviolet absorption and good visible transmission by using 3 to 6 per cent cerium dioxide and 0.2 per cent manganese dioxide with silica, potash, soda and lime. In another instance it was proposed to use as the only coloring oxide, 0.2 to 1 per cent

[17] French P. 720,075, July 16, 1931, to Deutsche Spiegelglas, A.-G.; *Chem. Abs.*, **26**, 3892 (1932).
[18] Taylor, W. C., U. S. P. 1,292,147 and 1,292,148, Jan. 21, 1919; *Chem. Abs.*, **13**, 1005 (1919).
[19] Taylor, W. C., U. S. P. 1,414,715, May 2, 1922; *Chem. Abs.*, **16**, 2206 (1922).

of ferric oxide, in making a glass which transmits no ultraviolet, but 84 per cent of the visible, through 2 mm.[20] To absorb both infrared and ultraviolet, not less than 0.3 per cent of cobalt and iron oxides, or 0.5 per cent of As_2O_3 and Sb_2O_3 may be added.[21] Cadmium sulfide and ferrous oxide have also been advocated.[22] A glass, said to be efficient in absorbing ultraviolet rays and practically colorless, is made by Chance Bros.[23] by using two or more ultraviolet-absorbing ingredients, the colors of which neutralize each other. A glass containing approximately 3.3 per cent of cerium and 0.7 per cent of didymium (added as oxides or hydroxides) is said to be practically colorless and efficient in absorbing ultraviolet rays. Another glass transmitting 80 per cent of visible light with but little selective absorption and cutting off all waves shorter than 3800A, contains a small proportion of chromium and vanadium.[24] E. A. Busch A.-G. Optische Ind.[25] colored lenses, regulating the tint as desired, by a suitable glaze, which might be applied only to the upper edge of the glasses, through which it was stated the dangerous rays usually enter the eye. The firm of Zeiss[26] described a glass which greatly weakens rays between 7000 and 15,000A and those below 3600A, while transmitting the visible range. Frank[27] adds to the glass batch a small quantity (0.00256 part by weight) of a mixture of MnO_2, 3 and Fe_2O_3, 2 parts. A thickness of 1.5 mm. absorbs a large proportion of ultraviolet and infrared rays without appreciably reducing the visible. Also, it is stated that laminated glass, with intervening sheets of celluloid or the like, may be made to exclude ultraviolet.[28]

A simple means of evaluating eye-protective glasses was proposed by Bloch.[29] In the ultraviolet (isolated by a "black glass" filter of the Sendlinger Optischer Glaswerke), the transmission of a standard quartz lamp light is estimated from the degree of fluorescence excited on a standard test paper. The results agree well with spectrographic determinations.

Starkie and Turner[30] in transmission studies of sections cut from commercial food containers and ground to 2 mm. thickness, demonstrated a rather definite increase in absorption with rise of the content of ferric oxide. Titanium dioxide also absorbs ultraviolet light, but the amounts found in commercial glasses, usually below 0.02 per cent are too small to function greatly.[31] Translucent sheets of cellulose hydrate are rendered impermeable to ultraviolet rays by treatment with aqueous pine bark extract, according to Gerngross and Callo.[32]

[20] French P. 760,998, March 7, 1934, to Pittsburgh Plate Glass Co.; *Chem. Abs.*, **28**, 4195 (1934).
[21] German P. 550,782, May 6, 1927, to Deutsche Spiegelglas A.-G.; *Chem. Abs.*, **26**, 4929 (1932).
[22] French P. 752,615, Sept. 27, 1933, to Verreries de Goetzenbruck; *Chem. Abs.*, **28**, 1160 (1934).
[23] Gell, P. V. W., Gould, C. E., Hampton, W. M., and Martin, H. S., U. S. P. 1,634,182, June 28, 1926, to Chance Bros. & Co., Ltd.; British P. 256,737, June 5, 1925; *Brit. Chem. Abs.*, **B**, 878 (1926); *Chem. Abs.*, **21**, 2775 (1927).
[24] Gould, C. E., British P. 316,464, Sept. 8, 1928, to Chance Bros. & Co., Ltd.; *Brit. Chem. Abs.*, **B**, 816 (1929).
[25] German P. 424,811, Jan. 10, 1925, to E. A. Busch, A.-G. Optische Ind.; *Brit. Chem. Abs.*, **B**, 789 (1926).
[26] British P. 252,130, May 16, 1925, to Firm of C. Zeiss Co.; *Chem. Abs.*, **21**, 1528 (1927).
[27] Frank, I., U. S. P. 1,615,448, Jan. 25, 1927; *Brit. Chem. Abs.*, **B**, 365 (1927); Chem. Abs., **21**, 808 (1927).
[28] Murray, G. H., U. S. P. 1,958,013, May 8, 1934; *Chem. Abs.*, **28**, 4196 (1934).
[29] Bloch, L., *Gas und Wasserfach.*, **70**, 1229 (1927); *Chem. Abs.*, **22**, 850 (1928); *Brit. Chem. Abs.*, **B**, 231 (1928). See also Danckwortt, P., and Jürgens, E., *Arch. Pharm.*, **272**, 713 (1934).
[30] Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.*, **12**, 27 (1928); *Chem. Abs.*, **22**, 2821 (1928).
[31] Smith, A. W., and Sheard, C., [*J. Opt. Soc. Am.*, **2**, 26 (1919)] gave earlier work on the absorption of ultraviolet light by glasses.
[32] Gerngross, O., and Callo, A., U. S. P. 2,106,599, Jan. 25, 1938; *Chem. Abs.*, **32**, 2654 (1938).

Glasses Permeable to Ultraviolet Radiations

After the discovery of the antirachitic properties of the ultraviolet rays of sunlight (Chapter 38), glass manufacturers sought to develop glasses capable of transmitting all the health-giving solar rays which reach the earth. For use in optical instruments, ultraviolet transmitting glasses had been, however, produced much earlier (about 1907) and Schott and Co. early marketed Uviol glasses, which were, unfortunately, expensive and unstable.[33] According to the historical summary by Davidovitch,[34] Eder and Valenta [35] pointed out that phosphate crown glass has a considerable transparency in the ultraviolet. Zschimmer [36] found that barium oxide had similar properties, but that glasses should be free from alkali metal oxides to increase ultraviolet transparency.[37] Sodium oxide glass is less transparent than that with potassium oxide. Glass with lead oxide is especially poor. Fritsch [38] found a generous proportion of B_2O_3 to confer excellent transparency. A glass of 6 parts of calcium fluoride and 14 of B_2O_3 was said to be transparent down to 1850A. Such glasses have been employed in spectrographic optical systems. Lithium glasses are said to be very transparent to short wave-lengths, but are unstable. While developing certain blue glasses, Luckiesh [39] noticed that cobalt glass appeared to be more transparent than clear glass in the region of 3000A.

Sugie [40] after investigation of the ultraviolet absorption of over fifty samples of soda-lime glasses, found no systematic relation between the absorption and the composition of the glass. Substituting sodium by potassium did not alter the transmission. Phosphorus pentoxide had no effect, but Sb_2O_3, TiO_2, Fe_2O_3, MgO and Al_2O_3 decreased the penetration. His most transparent glass had the composition: Na_2O, 1, CaO, 1.4 and SiO_2, 6 parts; this transmitted through 1.5 mm. wave-lengths as short as 2370A. The least transparent of his series had 1.5 parts of CaO and transmitted down to 2790A. It must be noted, however, that the shortest wave-length which gets through is not as significant a criterion of the quality of a glass as are the fractions of the incident radiation of various wave-lengths which are transmitted. This is true because the drop in the transmission curve is usually not sharp, but extends over several hundred Ångström units in many cases. Sugie found also that up to a certain point, nickel makes glass more transparent to the ultraviolet. When potash rather than soda is present, a nickel glass is black, although it transmits in the ultraviolet. Cobalt can be substituted for nickel in such glasses, but the use of both cobalt and nickel in the same glass diminishes the ultraviolet transmission. In soda-lime (but not potash-lime) glasses, ferric iron lowered the penetrability more than did ferrous iron. Chromium in small quantities had little effect. The effect of manganese is slight up to, but great above, 1 per cent.[41] Locke used a high proportion of alumina and avoided alkalies. In general, permeability increases with the silica content. Barium oxide is superior to lime which, in turn, is better than zinc oxide.

One of the more important lines of development which made possible the commercial production of ultraviolet glasses has been the reduction of those impurities in the raw materials, notably ferric and titanium oxides, which are recognized as increasing the ultraviolet absorption of ordinary silicon-lime-alkali glasses. Hadden [42] produced a glass (4 mm. plates of which are transparent to light waves shorter than 3000A) by reducing the iron impurities to less than 0.055 per cent (as ferric oxide) and the titanium oxide to less than 0.050 per cent. The melting was carried out in a crucible free from these oxides, under non-oxidizing conditions, *e.g.* in the presence of carbon, chromium, uranium, vanadium or nickel. The glass (980A) has a density 2.64 and a refractive index 1.539. The cost of production was above that of window glass, but far below that of quartz.[43] The Corning Co. makes a series of such Corex glasses. According to Gibson of the Bureau of Standards [44] 2 mm. sheets transmit 86 per cent of the radiations at 2900A. This figure is uncorrected for reflection losses of approximately 8 per cent. Corex is available either polished or unpolished, the latter having the same ultraviolet transmission, but not affording clear vision. A change of thickness does not greatly alter the transmission in the biologically important range between 2900 and 3100A.[45] The deleterious effect of ferric oxide was also recognized by Fuwa and Hiraoka,[46] who found the shortest wave-length transmitted by 4.30 mm. of a plate glass containing 0.090 per cent of the oxide to be 3021A. Only 3065A was transmitted by a much thinner plate, 2.78 mm., of a window glass containing 0.103 per cent iron oxide. Starkie and Turner [47] concluded from an extrapolation of their results on the transmission of glasses containing from 0.005 to 1 per cent of iron oxide, that the limiting transmission of a glass free from iron oxide would be 2230A.[48] Klumb and Hasse[49] proposed the use of very thin (10μ) glass windows for scientific work in the ultraviolet region.

By 1926, there had appeared on the market "Vitaglass," probably the first ultraviolet-transmitting glass manufactured in panes on a large scale.[50] The glass was developed by Lamplough, of Trinity College, Cambridge,[51] and was claimed to transmit about 40 per cent of all incident energy in the region 3130 to 2900A. Commercial production began in 1924 in the works of Chance Bros. & Co. and was later

[33] Rüttenauer, A., *Sprechsaal,* **61,** 449,453 (1928); *Chem. Abs.,* **23,** 2543 (1929).

[34] Davidovitch, P., *J. Opt. Soc. Am.,* **20,** 627 (1930).

[35] Eder, J. M., and Valenta, E., *Denkschriften, Wiener Akad. Wissenschaften Math. Nat. Kl,* **61** (1894).

[36] Zschimmer, E., *Z. Instrumentkunde,* **23,** 360 (1903).

[37] Zschimmer, E., *Physik. Z.,* **8,** 611 (1907).

[38] Fritsch, C., *Physikal. Z.,* **8,** 518 (1907).

[39] Luckiesh, M., *J. Frank. Inst.,* **186,** 111 (1918).

[40] Sugie, S., *Rept. Osaka Ind. Research Lab.,* **5,** No. 11, 1-26 (1924); No. 15, 1-19; **6,** No. 4, 1-26; *Chem. Abs.,* **20,** 3218 (1926).

[41] For further chemical data, see Locke, F. M., *Glass Ind.,* **7,** 136 (1926); *Chem. Abs.,* **21,** 3435 (1927); Weidert, F., *Sprechsaal,* **64,** 992 (1932); Jaeckel, G., *Z. tech. Physik,* **7,** 301 (1926); *Chem. Abs.,* **20,** 3066 (1926); Gilard, P., Swings, P., and Hautot, A., *Rev. belg. ind. verrieres,* **2,** 2, 26, 50, 74, 98 (1931); *Bull. sci. Acad. Roy. Belg.,* **17,** 235, 362 (1931); **15,** 749 (1929); *J. Soc. Glass Tech.,* **15,** 488; *Chem. Abs.,* **26,** 6086 (1932); Fromberg, B. M., and Oshchipkov, F. P., Russian P. 44,317, Sept. 30, 1935; *Chem. Abs.,* **32,** 3112 (1938).

[42] Hadden, R., British P. 263,410, July 1, 1926; 298,908, Oct. 5, 1927; 319,337, Sept. 27, 1928, to Corning Glass Works; *Chem. Abs.,* **22,** 148 (1928).

[43] Hood, H. P., *Science,* **64,** 281 (1926); *Chem. Abs.,* **20,** 3788 (1926); U. S. P. 1,830,902-4, Nov. 10, 1931. The yellow color may be eliminated by including a compound of zinc. The percentage of silica and B_2O_3 should be 10 to 22 times the total percentage of alkalies and the ratio of SiO_2 to B_2O_3 greater than 5. [German P. 637,438, Oct. 28, 1936.]

[44] Gibson, K. S., *J. Opt. Soc. Am.,* **13,** 279 (1926).

[45] One way of purifying the raw materials might be to obtain the silica by precipitation from industrial solutions of soluble glass, washing it free from the impurities with sulfuric acid containing hydrogen peroxide. "Osa" participations industrielles, French P. 760,329, Feb. 20, 1934; *Chem. Abs.,* **28,** 3549 (1934). For use of other reagents, see Düsing, W., and Enss, J., German P. 593,687, March 1, 1934; *Chem. Abs.,* **28,** 3549 (1934); Enss, J., and Hüniger, M., U. S. P. 2,107,935, Feb, 8, 1938, to General Elec. Co.; *Chem. Abs.,* **32,** 2703 (1938).

[46] Fuwa, K., and Hiraoka, T., *J. Japan. Ceram. Assoc.,* **34,** 504 (1926); *Chem. Abs.,* **22,** 487 (1928).

[47] Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.,* **12,** 324 (1928); *Chem. Abs.,* **23,** 3550 (1929); see also *J. Soc. Glass Tech.,* **15,** 365 (1931); *Chem. Abs.,* **26,** 3635 (1932).

[48] A number of general review articles covering in more detail the manufacture of special ultraviolet transmitting and absorbing glasses are available: English, S., *Brit. J. Radiol.,* **4,** 724 (1931); Wolf, J., *Ceram. et Verrerie,* 381 **(1931);** Hoffmann, J., *Sprechsaal,* **65,** 591 (1932); le Braz, J., *Glaces et Verres,* **5,** No. 27, 12 (1932); Grant, J., *Glass,* **9,** 391 (1932); Salmony-Karsten, A., *Chem. Ztg.,* **52,** 269 (1928); *J. Chem. Ind.,* **47,** 36,936 (1928).

[49] Klumb, H., and Hasse, T., *Z. Physik,* **76,** 322 (1932).

[50] *Chem. Age* (London), June 19, 545 (1926).

[51] Lamplough, F. E., *Pottery Gazette,* **54,** 1120 (1929).

extended to the works of Pilkington Bros., Ltd. The absorption by thin glass is shown in Figure 87. Tisdall and Brown [52] found "Vitaglass" to transmit approximately one-fourth of the antirachitic rays of December sunlight.

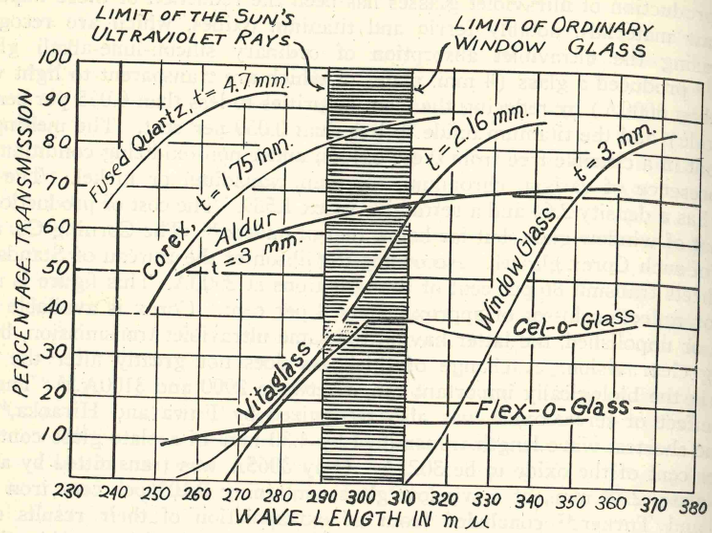


FIGURE 87. Transmission Curves for Vitaglass and Aldur (R. H. Crist, *Industrial and Engineering Chemistry*).

It must be remembered in connection with the use of ultraviolet-transmitting glasses that their effectiveness in the prevention of rickets is limited by the intensity of the incident radiation. If seasonal and atmospheric conditions, or dirt upon the glass, preclude the incidence of more than small quantities of energy in the desired wave-length band upon the glass surface, it is obvious that helpful results cannot be expected from its use. Dust and dirt may reduce the transmission at 3020A by 30 to 40 per cent. There is comparatively little of the valuable ultraviolet in the sunlight of Chicago during the winter months.[53] Clark [54] estimated that a person would receive as much ultraviolet radiation in two minutes in direct sunlight at noon, as in an entire day at 5 meters behind a window of ultraviolet-transmitting glass exposed to the north sky, because the amount of ultraviolet which can enter an ordinary-sized window represents such a small part of that which is available from the entire sky.[55]

Others have attempted to make ultraviolet-transmitting glasses by increasing the silica content of an ordinary glass, *e.g.*, the Quartzlite. Lai and Silverman [56] found the ultraviolet transmission of certain beryllium glasses to be greater than that of ordinary glass, but less than that of magnesium glass. Transmission decreases with

[52] Tisdall, F. F., and Brown, A., *Proc. Soc. Exptl. Biol. Med.*, **24**, 449 (1927).

[53] Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assn.*, **89**, 187 (1928).

[54] Clark, J., *Science*, **68**, 165 (1928).

[55] See also Eisenberg, K. B., *Gesundheit Ing.*, **51**, 465 (1928); *Chem. Abs.*, **22**, 3477 (1928); Long, B., *Science ind.*, **12**, 13 (1928).

[56] Lai, C., and Silverman, A., *J. Am. Ceram. Soc.*, **11**, 535 (1928); *Brit. Chem. Abs.*, **B**, 895 (1928); *Chem. Abs.*, **22**, 3271 (1928).

increasing beryllia content. Gould, Hampton and Martin [57] suggested the use of a batch giving a finished glass substantially free from dissolved gaseous oxides. The batch may comprise silica, borax and a powdered metal such as zinc, aluminum or tin which combines readily with oxygen and acts as a reducing agent.

English [58] gave a description of the experimental glasses which led to the development of Holviglass. Not only was the effect of iron considered, but it was stated that the admixture of either soda, potash or boric oxide with silica seriously reduces transmission by the latter. The best results were obtained with a soda-boron-silica glass, no relation between silica content and transparency being found. Alkali added as carbonate proved better than when added as the sulfate or nitrate.

Other manufacturers were concerned with the valence state of the iron oxide in the glass. Phelps [59] converted nearly all the iron in the glass to the ferric form by melting the glass under oxidizing conditions or by introducing a nitrate. This is at variance with the conclusions of many others, as Turner [60] who found for glasses containing 0.1 per cent of iron oxide a difference in transmission limits of about 100A between glasses containing the oxide in the ferrous and ferric states, the ferrous transmitting the better. Rose [61] found triavalent iron to cause the absorption of 100 times more ultraviolet than ferrous iron, the limits of transmission being at 3200 and 2200A, respectively.

Various reducing agents have been employed, as charcoal, which tends to make a muddy glass, zinc chloride [62] which makes the glass hazy, stannous oxide [63] or organic compounds such as urea.[64] Aluminum or magnesium powders have been proposed.[65] The addition of manganese oxide has been suggested on the ground that it undergoes oxidation in preference to the iron. Jaeckel [66] describes a glass of high transparency to ultraviolet rays containing at least 10 per cent BaO and not more than 10 per cent of B_2O_3 and not more than 3.5 moles of acid per mole of base. The glass contains no arsenous oxide and practically no ferric oxide. The N.V. Philips' Gloeilampenfabrieken [67] describes a glass substantially free from alkali oxide, consisting of at least 60 per cent of silica together with B_2O_3 and Al_2O_3. The glass softens above 600°. One proposed composition is SiO_2 77.2, Al_2O_3 10.7, CaO 5.4 and B_2O_3 7.0 per cent. Smelt [68] however, uses SiO_2 65, B_2O_3 2, Na_2O 5.5, K_2O 9.5, BaO 15 and ZnO about 3 per cent; iron (in traces) and a fluoride about 1 per cent were incorporated in the mixture.

Beryllium fluoride glasses have been said to transmit to 2200A [69] and Ziegler

[57] Gould, C. E., Hampton, W. M., and Martin, H. S., British P. 312,728, March 19, 1928; *Chem. Abs.*, **24**, 937 (1930).

[58] English, S., *Glass*, **5**, 338 (1928); **8**, 52 (1931); *Chem. Abs.*, **23**, 252 (1929).

[59] Phelps, D. V., British P. 320,904, July 25, 1928, to Pilkington Bros.; *Chem. Abs.*, **24**, 2566 (1930).

[60] Turner, W. E. S., *J. Soc. Chem. Ind.*, **48**, 65T (1929); *Chem. Abs.*, **23**, 3063 (1929); *Brit. Chem. Abs.*, **B**, 355 (1929); see also Andresen-Kraft, C., *Glastech. Ber.*, **9**, 577 (1931).

[61] Rose, G., *Sprechsaal*, **62**, 314, 333, 352, 375 (1929); *Chem. Abs.*, **23**, 4544 (1929).

[62] German P. 493,857, Dec. 30, 1925, to Deutsche Spiegelglas A.-G.; *Chem. Abs.*, **27**, 578 (1933).

[63] German P. 528,394, July 9, 1929, to Deutsche Spiegelglas A.-G.

[64] German P. 524,374, May 10, 1927, to Deutsche Spiegelglas A.-G.

[65] Vargin, V. V., *Keram i Steklo*, **7**, No. 1, 4 (1931); Wollner, F., Wollner, R., and Nikolai, F., British P. 339,903, March 12, 1929; Austrian P. 120,674, Oct. 15, 1929; French P. 691,805, March 12, 1930.

[66] Jaeckel, G., German P. 583,001, Aug. 26, 1933, to Sendlinger optische Glaswerke; *Chem. Abs.*, **28**, 277 (1934).

[67] British P. 440,778, Jan. 6, 1936, to N. V. Philips' Gloeilampenfabrieken; see also, Elenbaas, W., Jonas, G. B., and van Wyk, A., Canadian P. 373,786, May 17, 1938; *Chem. Abs.*, **32**, 5316 (1938).

[68] Smelt, J. A. M., U. S. P. 2,056,627, Oct. 6, 1936; *Chem. Abs.*, **30**, 8550 (1936).

[69] Heyne, G., *Angew. Chem.*, **46**, 473 (1933); Salmony-Karsten, A., *Sklarske Rozhledy*, **11**, 35 (1934); *Chem. Abs.*, **29**, 6713 (1935).

and Wellmann [70] have suggested alkali-beryllium-borate glasses as substitutes for quartz in optical work. Such a glass, containing 15 to 25 parts of boric acid, 1 to 2 of beryllium carbonate and an alkali carbonate equivalent to 3 to 6 parts of lithium carbonate, is reported to be applicable for lenses, prisms and mercury-vapor lamps. Draisbach and Draisbach [71] fuse beryllium ortho- or meta-phosphate, and add the corresponding salts of calcium, magnesium or sodium.

Another trend is the development of lithium-beryllium-borate "Getan" glass, which is not hygroscopic and does not decompose in the air, but is transparent to ultraviolet and x-rays.[72] One mm. of the glass transmits 80 per cent of the energy of the wave-length 2537A.

The Philips Lamp Co.[73] suggest for bulbs for transmitting ultraviolet a clear, transparent glass containing a fluoride and practically free from lead, antimony or titanium. Locke and Locke [74] melt a fluorine-containing batch (SiO_2 35.5-40, H_3BO_3 16.5-32.5, Al_2O_3 21-27 and CaO 11-17 per cent with calcium fluoride) in a carboniferous container. Fuwa and Suzuki [75] use 1 to 5 per cent sodium fluoride and 1 to 5 per cent ammonium oxalate or tartrate.

A glass of high resistance to water and permeable to the ultraviolet may be composed for the greater part of barium metaphosphate, along with metaphosphates of calcium and magnesium.[76] Grimm and Huppert [77] replace the silica normally used in making glass wholly or in part by $AlPO_4$ in the proportion of one molecule for every two of silica replaced. Ammonium salts, particularly phosphates, may be added to the frits of phosphate glass.[78]

Other Ultraviolet-Transmitting Materials. In the preparation of window-glass substitutes, materials quite unlike glass have at times been employed. Thus a urea-formaldehyde condensation product was introduced for this purpose by the Luco Products Corporation under the name of Aldur. Crist [79] gave a curve for its transmission and compared it with "Vitaglass." (Figure 87.) He found also that when exposed at 65°C. at 8 inches from a 220-volt mercury lamp, no change in transmission of the 3020A region was apparent after 41 hours, a fairly severe test. The transmission of the 2540A line was decreased from 48 to 40 per cent in 18 hours. Data for "Plexiglas" (Acryloid) have been given by Jakobson.[80]

A filter suitable for glazing windows which transmits to 2900A is a polymerized vinyl acetate, reënforced with a reticulated material as a wire mesh or woven

[70] Ziegler, W., and Wellmann, M., *Z. tech. Physik*, **14**, 288 (1933); *Chem. Abs.*, **27**, 4366 (1933); Wellmann, M., German P. 585,816 (1933); *Chem. Abs.*, **28**, 1492 (1934).

[71] Draisbach, H., and Draisbach, F., British P. 436,426, Oct. 10, 1935; French P. 785,966, Aug. 23, 1935.

[72] Hertsriken, S. D., *Tech. Phys. U.S.S.R.*, **3**, 336 (1936); *Chem. Abs.*, **31**, 4782 (1937).

[73] British P. 373,378, May 29, 1930, to N. V. Philips' Gloeilampenfabrieken; *Chem. Abs.*, **27**, 3306 (1933).

[74] Locke, F. M., and Locke, F. J., U. S. P. 1,886,280, Nov. 1, 1932, to Corning Glass Co.; *Chem. Abs.*, **27**, 1470 (1933).

[75] Fuwa, K., and Suzuki, S. Japanese P. 101,817, July 1, 1933; *Chem. Abs.*, **28**, 5617 (1934); Fuwa, K., U. S. P. 1,971,309, Aug. 21, 1934, to General Electric Co.; *Chem. Abs.*, **28**, 6542 (1934).

[76] French P. 751,524, Sept. 5, 1933, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, **28**, 1159 (1934); Kaufmann, W., and Bungartz, E., U. S. P. 2,031,958; German P. 634,698-9 and 636,035; *Chem. Abs.*, **31**, 828 (1937). Aluminum may also be added to increase the water resistance.

[77] Grimm, H. G., and Huppert, P., German P. 580,295, July 8, 1933; *Chem. Abs.*, **27**, 388, 4895 (1933).

[78] French P. 775,451, Dec. 28, 1934, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, **29**, 2680 (1935); British P. 424,366, Feb. 20, 1935. For other patents on ultraviolet glasses, see German P. 527,053, Dec. 16, 1928, to Deutsche Gasglühlicht Auer-Ges.; Gericke, I., German P. 527,404, Jan. 17, 1930; Weld, H. W., U. S. P. 1,845,376, Feb. 16, 1932; *Chem. Abs.*, **26**, 2294 (1932).

[79] Crist, R. H., *Ind. Eng. Chem.*, **20**, 1367 (1928); see also Katowaki, H., and Kasai, E., *Repts. Imp. Ind. Research Inst., Osaka*, **13**, No. 3 (1932); *Chem. Abs.*, **27**, 1719 (1933).

[80] Jakobson, T., *Tek. Tid.*, **67**, Uppl. A-C, Kemi, 15 (1937); *Chem. Abs.*, **31**, 4210 (1937).

fabric.[81] It has been proposed to make a fabric of threads formed of a core of material opaque to light, such as cotton, carrying a coating such as regenerated cellulose, capable of transmitting ultraviolet.[82] The Vitalite Co. produces a fine wire cloth coated with a cellulose acetate composition, yielding a flexible wire product, possessing the advantages of weather resistance and transmitting the ultraviolet range. Ramstetter [83] suggested the use of transparent condensation products of carbamide and its derivatives with substances capable of yielding formaldehyde as a substitute for quartz glass; the condensation products absorb ultraviolet rays but slightly. Walsh [84] coats a wire cloth with an ultraviolet-transparent film of cellulose acetate 100, triphenyl phosphate 10-20 and dibutyl tartrate 10 to 20 parts.

In some instances [85] "Vitaglass" or quartz glass may be made into a laminated glass by the aid of acetylcellulose applied in the form of thin sheets. Zimmerli [86] prepared an ultraviolet-transmitting material by evaporation of a cellulose ester and a plasticizer, such as diethyl phthalate. Polymerized vinyl compounds, including vinyl acetate, chloroacetate and styrene, may be used in single or laminated sheets in making reënforced glass substitutes permeable to ultraviolet light.[87]

Data on the Transmission of Various Ultraviolet-permeable Materials. Starkie and Turner [88] determined the transmissions of 2 mm. thicknesses of eight commercial glasses over the range 7000 to 2000A. Corex A was found to transmit 89 per cent in the therapeutic region (2950-3150A). The remaining glasses showed: "Sanalux," 73 per cent, "Sun Ray" 62, "Holvi" 61, "Viat" 54, "Helio" 53, "Uviol" 45, "Quartz-Lite," 4 per cent. Ordinary window glass transmits only 1 per cent of these rays. Corex had the lowest iron content, 0.012 per cent, that of the remaining samples ranging from 0.021 to 0.054 per cent. After a 12 weeks' exposure to sunlight, Corex became stained with a white film. But on being cleaned, it showed undiminished transmission. When artificially aged under the carbon arc, the greatest change occurred in the first two hours, the fall in transmission coinciding with a decrease in the proportion of ferrous oxide to total iron oxide in the glass. Turner [89] finds this change can be reversed by heating the glass to 600-700°C.[90] Hoffman [91] believes the solarization to incolve the formation of ferrites.

According to Bundesen, Lemon, Falk and Coade,[92] incandescent 300-watt lamps with ordinary glass bulbs emitted radiations comparable to Chicago sunlight in the winter months and Vitaglass bulbs emitted radiations as far as the region 2800 to 2900A.

The results of the physical transmission of Corex received confirmation in

[81] Greider, C. E., U. S. P. 1,786,205, Dec. 23, 1930, to National Carbon Co. Note also British P. 366,077, June 29, 1929.

[82] Millen, J., U. S. P. 1,910,850, May 25, 1933; *Chem. Abs.*, **27**, 4101 (1933).

[83] Ramstetter, H., German P. 416,753, Jan. 31, 1923, to Badische Anilin und Soda Fabrik.

[84] Walsh, J. F., U. S. P. 1,931,518, Oct. 24, 1933, to Celluloid Corp.; *Chem. Abs.*, **28**, 637 (1934).

[85] Colefax, M. A., British P. 323,671; *Kunstoffe*, June, 139 (1930). Dreyfus, C., U. S. P. 1,924,398, Aug. 29, 1933; *Chem. Abs.*, **27**, 5503 (1933); U. S. P. 2,002,082, May 21, 1935; *Chem. Abs.*, **29**, 4539 (1935); Canadian P. 330,842; *Chem. Abs.*, **27**, 3375 (1933); British P. 306,397, Feb. 18, 1928, to British Celanese, Ltd.; *Chem. Abs.*, **23**, 5021 (1929).

[86] Zimmerli, A., U. S. P. 1,842,640, Jan. 26, 1932, to Acetol Products; *Chem. Abs.*, **26**, 1781 (1932).

[87] British P. 366,077, July 29, 1929, to Celluloid Corp.; *Chem. Abs.*, **27**, 3047 (1933).

[88] Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.*, **12**, 306 (1928); *J. Soc. Chem. Ind. Supplement*, March 29, 245 (1929). Other data have been given by Winther, C., *Z. wiss. Phot.*, **25**, 230 (1928), and by Harris, D. T., *J. Sci. Instruments*, **6**, 2 (1929).

[89] Turner, W. E. S., *J. Soc. Chem. Ind.*, **48**, 65 (1929).

[90] Compare Hood, H. P., U. S. P. 1,889,067, Nov. 29, 1932; *Chem. Abs.*, **27**, 1470 (1933). British P. 298,908, Nov. 14, 1928, to Corning Glass Co.; *Chem. Abs.*, **23**, 3066 (1929). Hood heats to 550° for 15 minutes or to 400°C. for one hour.

[91] Hoffmann, J., *Glastech. Ber.*, **12**, 53 (1934); *Chem. Abs.*, **28**, 4554 (1934).

[92] Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assoc.*, **89**, 187 (1928).

prophylactic animal tests against rickets, using Uviarc irradiation through the samples.[93] Growth curves, calcium and phosphorus determinations in the blood serum, x-rays of the tibiae and femurs, bone ash and pathological studies agreed in showing that irradiation through Corex was as effective as direct irradiation. "Vitaglass" was less effective and animals irradiated through ordinary window glass gave results very similar to those found in non-irradiated animals. Wyman[94] also conducted therapeutic tests on rachitic children with similar results.

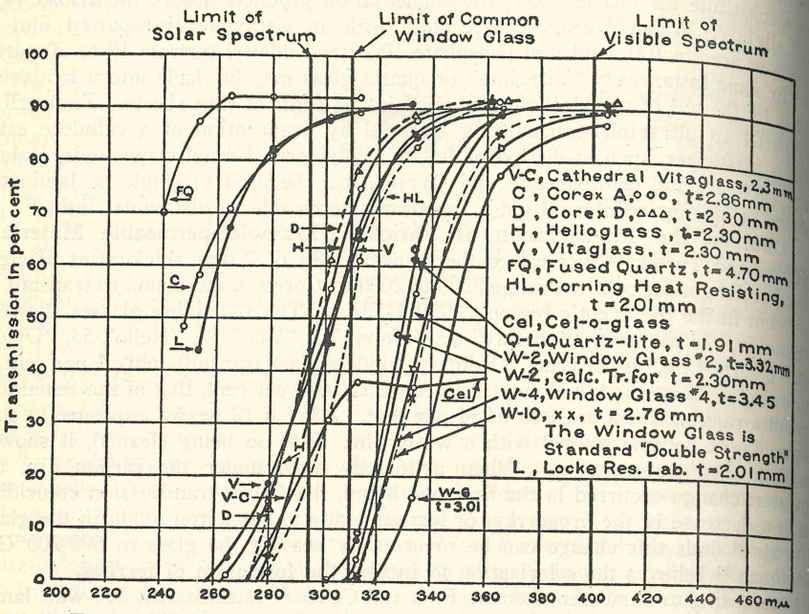


FIGURE 88. Transmission Curves of Ultraviolet-permeable Glasses. (Coblentz and Stair, *Journal Research, Bureau of Standards*).

Durability of Ultraviolet-transmitting Materials. The question of solarization, or the effect of prolonged exposure to the sun or other sources of ultraviolet is of importance since ultraviolet transmitting materials are intended for use over long periods. The discoloration of glass in the globes surrounding street arc lights is familiar to everyone. Eckert[95] noted that glasses containing a small percentage of cerium rapidly assume a brown color in day or artificial light due to the action of ultraviolet rays, the glass becoming fluorescent and phosphorescent. The brown color fades irreversibly on heating.

In 1927 the Bureau of Standards had found that nearly all of the glasses then in use undergo a photochemical action, the glass decreasing greatly in transparency in the region 2900 to 3100A when exposed to ultraviolet radiations.[96] The materials fell into three classes (Figure 88): (1) Fused quartz, Corex and Locke glass, which have an initial transmission of the 3020A line of over 85 per cent and show little or no decrease in solarization; (2) "Vitaglass" and Helioglass, with initial transmission of 45-55 per cent, decreasing to about half on exposure; (3) Quartz-lite and common window glass, with initial transmissions of 0 to 1.5 per cent and no change on exposure. Cel-O-glass becomes opaque to this line after 25 hours' exposure to the quartz mercury arc, but a sample that had been exposed to the sun for 400 hours during the months of April to October decreased but little in transparency. On the other hand, samples that had transmitted 30 per cent when new, transmitted only 5 to 10 per cent after having been exposed on the side of a building day and night from April to December, showing that the change in transparency may depend upon weather conditions. This product has been employed in poultry houses for preventing leg weakness in chicks.[97] Russell and Howard[98] found that the value of Cel-O-glass for this purpose was not diminished after exposure for 13.5 months.

In more recent work, Coblentz[99] reported improvement in the quality of certain of these glasses. He summarized data (based on samples secured prior to May 1, 1930) based on exposure of the glasses for ten hours at 15 cm. from a 110-volt, horizontal Uviarc and of duplicate samples exposed to the sun for five to twelve months, using an average thickness of 2.3 mm. (Table 15.)

Table 15.—Transmission of Ultraviolet Rays by Glass.

Trade Name	Number of Samples	Average Per Cent Transmission		
		New	After Uviarc	After Sun
Quartz glass	1	92	92	92
Corex D	3	61	59	60
Newglas	3	63	50	57
Uviol-Jena	3	67	48	53
Helioglass	8	64	45	53
Sunlit	3	71*	42*	51
Vitaglass	20	58	33	42
Common window	3	0	0	0

* Improved material later examined averaged 72 per cent when new and 47 per cent after exposure to the mercury lamp.

Rüttenauer[100] found the foreign products Osram UV, Ultraviol, Brephos, Bios, Vita and Schott's UV to show only small ageing. He has also considered the effect of heat on the rate of ageing, a matter of importance when such glasses are used in lamp bulbs. Nitchie and Schmutz[101] found in some cases an increase in short-wave transmission at 450°C.

Coblentz and Stair[102] studied the effects of various filtered ultraviolet wavelengths in producing changes in the ultraviolet transmission of soda-lime-silica glass. The work was done in the hope of accelerating stabilization of the transmission. This effort proved impracticable because of antagonistic effects about 3650A which

[93] Wyman, E. T., Holmes, A. D., Smith, L. W., Stockbarger, D. C. ,and Piggott, M. G., *Am. J. Diseases of Children*, **37**, 473 (1929); *Chem. Abs.*, **23**, 3064 (1929).

[94] Wyman, E. T., *Boston Med. & Surg. J.*, **197**, 376 (1927).

[95] Eckert, F., *Z. tech. Physik*, **7**, 300 (1926); Eckert, F., and Schmidt, K., *Glastech. Ber.*, **10**, 80 (1932); *Chem. Abs.*, **27**, 1468 (1933).

[96] Bureau of Standards, *J. Frank. Inst.*, 666 (1927); *Letter Circular No. 235, 3rd Revision; J. Research Bur. Standards*, **3**, 629 (1929); Coblentz, W. W., and Stair, R., *Trans. Illum. Eng. Soc.*, **23**, 1121 (1928); *Chem. Abs.*, **23**, 944 (1929).

[97] Cochran, R. L., and Bittenbender, H. A., *Bull. 246, Iowa State College, Agr. Expt. Sta.*, **1928**.

[98] Russell, W. C., and Howard, C. H., *Poultry Sci.*, **8**, 290 (1929).

[99] Coblentz, W. W., *Trans. Illum. Eng. Soc.*, **26**, 610 (1931).

[100] Rüttenauer, A., *Sprechsaal*, **61**, 449 (1928).

[101] Nitchie, C. C., and Schmutz, F. C., *Science*, **71**, 590 (1930).

[102] Coblentz, W. W., and Stair, R., *J. Research Bur. Standards*, **13**, 773 (1934); *Proc. Nat. Acad. Sci.*, **20**, 630 (1934); *Chem. Abs.*, **29**, 1597 (1935).

reversed the action of shorter wave-lengths. No wave-length shorter than 3650A was found to have the exclusive property of increasing or decreasing the ultraviolet transmission of these glasses. A phosphate-lime glass has its transmission lowered by wave-lengths shorter than 2900A, and this could not be retarded by exposure to the region 2970-3650A, in contrast to the soda-lime-silica glasses. Stockbarger[103] is of the opinion that solarization, at least so far as it relates to the application of ultraviolet glasses in photochemical apparatus, is not serious. Solarization takes place within a short length of time, after which the characteristic properties of the glass are retained for a considerable time. It has been said that when kept in the dark, glass, previously solarized by the mercury arc, does not regain any of its lost ultraviolet transparency, but that it does regain transparency when exposed to sunlight directly or through window glass or when exposed to the mercury arc through a thick layer of window glass. It is also pointed out[104] that the use of the mercury-vapor lamp to predict the loss of transparency of glass when exposed to sunlight may give misleading results.

The tendency of an ultraviolet-permeable glass to lose transparency may be counteracted by the incorporation of a small proportion (0.05-0.5 per cent) of manganese oxide.[105] The I. G. Farbenindustrie[106] describes an ultraviolet-permeable phosphate glass (stable to irradiation) which was said to have the following composition: potassium carbonate 13.77, potassium nitrate 6.71, calcium carbonate 8.93, barium carbonate 3.22, magnesium carbonate 18.53, B_2O_3 31.04, alumina 28.80 and secondary ammonium phosphate 48.70 parts. Huppert and Wolff[107] state that the important phosphatic glasses may be rendered more stable to radiations by including an ammonium salt (phosphate, carbonate or nitrate). The formation of blisters may be avoided by the addition of an oxidizing agent.

Lasse[108] finds irradiation of ordinary and Uviol plate glass with wave-lengths 3000 to 4000A from a Hanau silica burner diminishes the transparency for these rays to 34 and 19 per cent respectively. The coloration of manganese-containing glass by ultraviolet rays is said by Cross[109] to be due to light of a wave-length only slightly greater than 2900A, the absorption limit of the glass. The tinting takes place only near the surface, and is hastened by heating. Decolorization is accelerated by heat or visible light.

The fluorescent effects produced by ultraviolet on various glasses are sufficiently different to afford indications of the nature of their coloring materials.[110] Shrum, Patten and Smith[111] found heat treatment at 300°C. to remove the ability of ultraviolet light or even x-ray solarized glasses to luminesce before the quartz mercury arc. The transmission in the ultraviolet was restored as the thermoluminescence disappeared.[112]

[103] Stockbarger, D. C., *Science,* **70,** 73 (1929).

[104] Wood, A. R., and Leathwood, M. N., *Nature,* **124,** 441 (1929).

[105] British P. 291,468, June 4, 1927, to Soc. Anon. des Manufactures des Glaces et Produits Chimiques de Saint-Gobain, Chauny, et Cirey; *Chem. Abs.,* **23,** 1235 (1929); *Brit. Chem. Abs.,* **B,** 145 (1930); French P. 647,188, June 4, 1927; Long, B., U. S. P. 1,779,176.

[106] British P. 424,366, Dec. 2, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.,* **B,** 406 (1935).

[107] Huppert, P., and Wolff, H., German P. 630,347, Oct. 19, 1935; U. S. P. 2,077,481; see also Hoffmann, J., *Sprechsaal,* **70,** 517, 529 (1937); *Chem. Abs.,* **32,** 5592, 8717 (1938).

[108] Lasse, R., *Helv. Phys. Acta,* **5,** 92 (1932); *Chem. Abs.,* **26,** 6086 (1932).

[109] Cross, C. L., *Phys. Rev.,* **27,** 108 (1926).

[110] Lester, W. R., *Glass Ind.,* **12,** 83 (1931).

[111] Shrum, G. M., Patten, C. G., and Smith, H. D., *Trans. Roy. Soc. Canada,* **22,** (3), 433 (1928); *Chem. Abs.,* **23,** 2003 (1929).

[112] For further discussion of the theory of solarization processes, see Klemm, A., and Berger, E., *Glastech. Ber.,* **13,** 349 (1935); Hoffmann, J., *Ibid.,* **12,** 53 (1934); *Chem. Abs.,* **28,** 4554 (1934); *Glastech. Ber.,* **13,** 47 (1935); *Brit. Chem. Abs.,* **B,** 1093 (1936); *Glastech. Ber.,* **14,** 281 (1936); *Glass,* **13,** 419, 433 (1936).

Filters

In the visible region, a great number of screens or filters have been prepared for the isolation of definite wave-length regions; certain of these find wide employment in photography, especially in color photography. Others are of importance in stage lighting. The properties of these and other filters are due to the ability of the substances employed to absorb radiations of definite frequencies selectively. Substances which are highly absorbing even when present in extremely dilute solutions are the most satisfactory materials for filters since, when taken in higher concentrations, they exhibit a sharp cut-off of radiations transmitted. This means that the wave-length range between nearly complete transmission and nearly complete absorption is very narrow, comprising only a few Angström units. Since but few substances meet this requirement, filters are best used with discontinuous line sources of radiations as the mercury arc.

The theory of the application of glass filters to the measurement of the intensity of groups of lines emitted by a source has been discussed in detail by Stockbarger and Burns.[113] Errors may arise because of failure to take into account the fact that the transmission curves of filters are not rectangular but sloping; if the cut-off be taken as the wave-length at which the transmission becomes zero, the results will be greatly in error. These authors recommend that the effective "cut-off" be considered to be the point at which the energy transmitted by the filter below the "cut-off" equals that which is selectively absorbed above it. In order to locate this point there needs to be known, besides the transmission characteristics of the filter, the energy distribution of the source in the region in which the filter transmits poorly.

Particular attention has been devoted to the theory relating the slope of the absorption curve of a filter material to the effectiveness with which it will separate a given line from close neighboring lines, by Dahm,[114] who was especially interested in developing filters suitable for use in studies of the photoelectric effect. He gives absorption data for over twenty organic compounds, plotted in an unusual manner adapted to his theoretical treatment.

Stability is another quality desired in a filter material. The absorbed radiations must produce or initiate only very slow photochemical changes. Otherwise, the nature of the filtering material will change during its use, and the products formed may absorb quite differently, resulting in a change in the filtering properties with use. In the colored filters employed in the visible region, these changes are usually slow enough so that the filters are stable for considerable periods. Liquid filters composed of solutions of colored salts or dyes in cells with parallel glass sides, or solid filters of glass or stained films of collodion or more usually gelatin, are commonly employed. Simple inorganic salts when available are usually more stable and more readily prepared in definite concentrations than are the organic dyes, which may be of less definite purity and which are frequently subject to fading.

In the ultraviolet region, the energies associated with the various wave-lengths absorbed by the filters are far greater than in the visible region. In this region, therefore, it is necessary to check the filtering characteristics of filters at frequent intervals or else to use solutions which flow slowly through the filter cells.

Filters capable of transmitting only narrow spectral bands or individual lines are rare. It is usually necessary to use filters to supply radiations from which certain more or less broad spectral regions have been excluded. In the visible region, there is a filter arrangement which transmits only the green line of the mercury arc. This filter is didymium glass, which has a sharp absorption band

[113] Stockbarger, D. C., and Burns, L., *Phys. Rev.,* **34,** 1265 (1929).

[114] Dahm, T. M., *J. Opt. Soc. Am.,* **15,** 266 (1927).

between 5500 and 5800A. Used with a strong yellow filter, the filter yields the green line in high intensity and supplies a strong source of nearly monochromatic light. Glasses to emphasize color contrasts may contain neodymium oxide.[115] A discussion of filters in the infrared and visible regions lies beyond the scope of this book.[116] Many photographic filters have the drawback of fluorescing and so causing a loss of contrast.[117]

Filters for Black Light. Among the earliest ultraviolet filters were those designed to exclude the visible rays and transmit only the invisible ultraviolet. Such filters have recently acquired new importance with the development of methods of fluorescence analysis under ultraviolet irradiation. By their use, fluorescent effects in great variety are easily secured. In a darkened room irradiated only by ultraviolet rays, the teeth, eyes and even the fingernails glow with a weird yellowish fluorescence. Artificial teeth do not become fluorescent but appear black. The beautiful fluorescent effects characteristic of various minerals have been so frequently exhibited in museums as to be familiar to almost everyone. Uranium nitrate shines when exposed to ultraviolet rays, and vapors of mercury may be seen rising from a body of mercury even at room temperature when photographed by ultraviolet rays.

A filter for this purpose consisting of quartz coated with silver was employed by R. W. Wood in 1911 in a demonstration at the Royal Institution of the fluorescent effects produced by ultraviolet radiations. Among the striking effects there demonstrated was the fact that white zinc oxide comes out black. Photographs of flowers taken through a quartz lens were also exhibited. A number of flowers which, when photographed by visible light, came out in widely different shades, when white or colored, left a black or dark gray image when photographed by ultraviolet light. Another group of flowers to which Michaud and Tristan [118] gave the name of ultraviolet flowers, were reproduced by ultraviolet much as by ordinary light. These flowers were yellow under ordinary light. These authors prepared a lens which excludes light other than ultraviolet by precipitating on a quartz lens a layer of silver from an alkaline silver solution by means of a 10 per cent solution of milk sugar.

Silver, either in the form of plates or in the colloidal state, is not entirely satisfactory since its absorbing capacity ends at about 4000A [119] and with high concentrations of silver, absorption in the short ultraviolet region is noted. Brock [120] prepared a silver filter by exposing a lantern slide, developing it to a brown color and then stripping off the emulsion and supporting the latter between two plates of Uviol or "Vitaglass." The resulting filtering action is believed superior to that of either sputtered or chemically deposited films, maximum transmission occurring at about 3000A.

Wood [121] suggested the use of nitroso-dimethylaniline in making filters transparent only to ultraviolet rays. This compound, however, transmits only the longer

[115] Weidert, F., British P. 338,334, Dec. 15, 1928; *Chem. Abs.*, **25**, 2259 (1931).

[116] See Mees, C. E. K., in Glazebrook's Dictionary of Applied Physics, IV; Potapenko, G., *J. Russian Phys. Chem. Soc.*, **48**, 790 (1916); *Brit. J. Phot.*, **68**, 507 (1921).

[117] Bäckström, H., and Johansson, R., *Z. wiss. Phot.*, **36**, 194 (1937); *Chem. Abs.*, **31**, 6123 (1937); **32**, 2837 (1938).

[118] Michaud, G., and Tristan, F., *Scientific American*, **111**, 301 (1914).

[119] See also Goos, F., *Z. Physik*, **100**, 95 (1936); for gold films, see Goos, F., *Z. Physik*, **100**, 606 (1937).

[120] Brock, G. C., *Sci. Proc. Roy. Dublin Soc.*, **20**, 563 (1933); *Brit. J. Phot.*, **80**, 495 (1933); *Chem. Abs.*, **27**, 5262 (1933).

[121] Wood, R. W., *Phil. Mag.*, **5**, 257 (1903); see also Lehmann, H. *Physik. Z.*, **11**, 1039 (1910).

ultraviolet. Absorption spectra for the aniline derivative and for methyl violet have been determined by Pospelov and Yampolskii.[122]

Winther and Mynster [123] suggested a filter which transmits a range of 4050 to 3200A with a maximum at 3750A. It consists of a one centimeter cell containing a 2.5 per cent solution of copper sulfate with six times the quantity of ammonia necessary to redissolve the precipitate which first forms. This is combined with a one centimeter cell of a 0.045 per cent solution of fuchsine in water. In another filter, the dye is replaced by a 0.1215 per cent solution of potassium chromate, the maximum transmission in this case being at 3130A. With an increasing excess of ammonia, copper sulfate solution becomes more transparent, especially in the ultraviolet; the maximum transparency is attained when the ammonia present is four times the quantity necessary to redissolve the precipitated copper hydroxide, and then extends from 4500 to 3000A.

Lamps in Corex are made impermeable to visible rays, while retaining their ultraviolet transmission, by dipping in an alcoholic suspension of P_2O_5 68, CaO 27, B_2O_3 5 per cent, with cobalt oxide to color, or of SiO_2 68.5, B_2O_3 23, Na_2O 6.5 and Al_2O_3 2 per cent. The lamps are then heated in a furnace.[124] An envelope to serve this same purpose has been suggested by Gillard and West.[125] It comprises glass with nickel oxide and a little copper oxide. The maximum transparency is at 3650A, falling rapidly on either side of this wave-length. Another means of securing ultraviolet radiation with but one per cent of the visible is by operation of a small mercury arc at 5 amperes and 15 volts.[126]

Filters Excluding Various Ultraviolet Regions. Some of the glasses whose transmission characteristics have been discussed in the preceding section, have been employed as filters for various wave-lengths in the ultraviolet region. Their usefulness for this purpose is somewhat limited by the lack of sharpness of their transmission curves.[127]

Corning glass filters [128] are most satisfactory where their thickness and consequent bulk are not objectionable, and where appreciable heat must be dealt with. As is apparent from Figure 89, they generally have rather broad but high transmission characteristics and hence are used in combination to secure the desired effects. A nickel oxide glass (Corning) transmits 3660A. Further data on the filtering properties of various glasses by Taylor and Holladay are recorded in Figure 90.[129]

In order to prepare a ray filter which will allow only waves of a definite length to pass, Peskov [130] states that it is necessary to calculate the coefficient of absorption of the substance and then determine the density and thickness of the solution so that the desired quantity of energy of a definite wave-length will pass the filter.

Gases have been widely used as filters in the ultraviolet. The coefficients of absorption of a number of gases for light after passage through quartz windows has been measured by Varley.[131] It is the filtering characteristic of oxygen (aside

[122] Pospelov, A., and Yampolskii, B., *J. Phys. Chem. (U.S.S.R.)*, **3**, 514 (1932); *Chem. Abs.*, **27**, 1826 (1933).

[123] Winther, C., and Mynster, E. H., *Z. wiss. Phot.*, **24**, 90 (1926); *Chem. Abs.*, **20**, 3249 (1926).

[124] French P. 762,053, April 3, 1934, to Compagnie des lampes. See also Eidinow, A., and Hewittic Electric Co., Ltd., British P. 307,961, Dec. 13, 1927; *Chem. Abs.*, **24**, 29 (1930).

[125] Gillard, F. W., and West, D. L., British P. 294,949, Apr. 1, 1929; *Chem. Abs.*, **23**, 1827 (1929). Note also Sugie, J., *J. Japan. Ceram. Assoc.*, **34**, 24 (1926); *Chem. Abs.*, **22**, 487 (1928).

[126] Zahour, R. L., *Elec. J.*, **30**, 453 (1933).

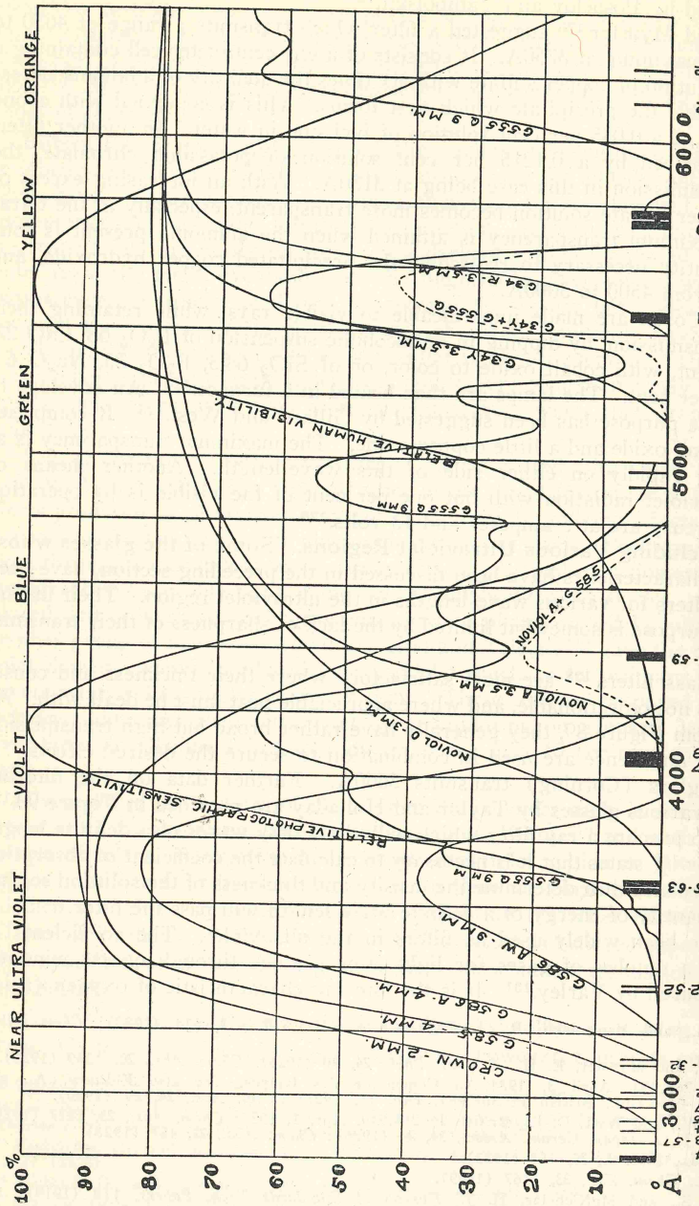
[127] Mannich, C., *Chem. Ztg.*, **33**, 1167 (1909).

[128] Gibson, K. S., and McNicholas, H. J., *Bureau of Standards Tech. Papers*, 119 (1919); 148 (1920); *Sci. Paper* 325 (1918).

[129] Taylor, A. H., and Holladay, L. L., *Trans. Illumin. Eng. Soc.*, **26**, 711 (1931).

[130] Peskov, N. P., *J. Phys. Chem.*, **21**, 381 (1917); *Z. wiss. Phot.*, **18**, 235 (1919).

[131] Varley, W. M., *Proc. Camb. Phil. Soc.*, **12**, 510 (1904).



CORNING FILTERS - DATA FROM CORNING GLASS WORKS AND BUREAU OF STANDARDS. (Courtesy, Cooper-Hewitt Electric Co.)

FIGURE 89. Transmission Curves for Corning Glass Filters.

from the limitations of the output of the source employed) which sets the short wave limit in most photochemical work, since it begins to absorb strongly at 1860A, while nitrogen is transparent even at 1250A. According to Peskov, chlorine is frequently useful, since its maximum absorption is in the region 3800-3000A. Bromine vapor cuts out the visible part of the spectrum to 3800A and its absorption capacity ends slightly beyond the point where chlorine absorption begins.[132] In water solutions, the absorption characteristics of these two elements change because of the formation of complex molecules of halogen and water.

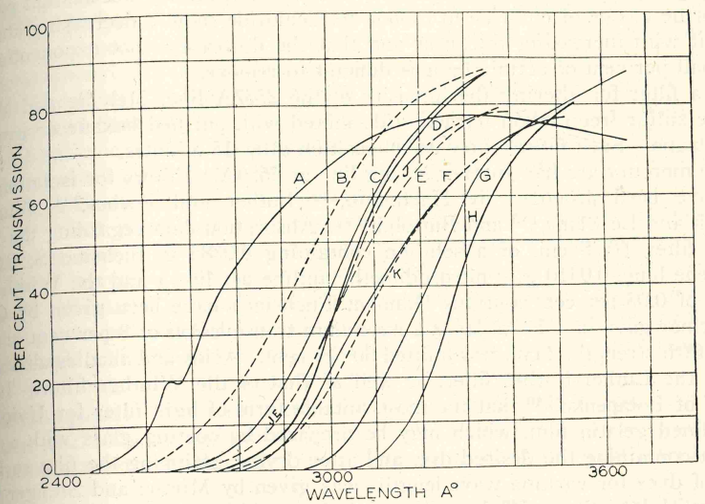


FIGURE 90. Spectral Transmission Curves of Glass Filters (Taylor and Holladay, *Transactions Illumination Engineering Society*). A, red-purple Corex A, 4.21 mm. thick; B, microscope glass, 0.18 mm.; C, microscope slide, 0.96 mm.; D, "Pyrex," 1.05 mm.; E, 2 layers of microscope glass, 0.36 mm. total; F, 3 layers of microscope glass, 0.55 mm. total; G, "Pyrex," 2.99 mm.; H, Quartzlite, 2.02 mm.; J, Helioglass, 2 mm.; K, "Vitaglass," 2.77 mm.

Use has been made of chlorine and bromine filters in the work of Svedberg and Nichols[133] on the determination of the molecular weight of egg albumin by ultracentrifugal methods. In this work, it was necessary to determine the concentration of the protein solution at various parts of a quartz cell by a photographic method depending upon the property of the protein to absorb in the ultraviolet. In order to measure the concentration of the protein by means of the density of a photograph obtained by passing light from a mercury arc through the solution, it is necessary that a strong absorption band of the protein be used. Since the protein does not absorb much light of wave-lengths longer than about 2950A, it is necessary that such light be removed by a filter to prevent the light from affecting the photographic plate. A combination of chlorine and bromine filters absorbs most rays longer than 2950A and passes those shorter. Although the filter does not remove the yellow mercury line, this does not affect the photographic plate.

To obtain the 2537A line alone by methods other than the use of special reso-

[132] Oldenberg, O., *Z. Physik*, **29**, 328 (1924).
[133] Svedberg, T., and Nichols, J. B., *J. Am. Chem. Soc.*, **48**, 3085 (1926).

nance lamps, it has been proposed to use the halogens at higher concentrations. Peskov [134] calculated from their extinction coefficients that the bromine should be about 0.0046 molar and the chlorine 0.176 molar or about 4 atmospheres. Oldenberg [135] proposed to avoid any absorption of the 2537A line by bromine [136] by omitting the latter and employing chlorine at a pressure of 6.5 atmospheres. Such high-pressure filter cells have been constructed of quartz. The absorption of the chlorine filter has been measured by Villars.[137] Calculations showed the Peskov filter would be the more nearly monochromatic and would transmit about 27 per cent of the light incident at 2537A. Taylor [138] states that filters (not at high pressure) of chlorine gas or of chlorine in carbon tetrachloride show a decreasing absorption per unit with increasing thickness and that the decrease is not exponential. The last small per cent of actinic light is difficult to remove.

As a filter for altering the intensity of the 2537A line, Melville and Walls [139] propose sulfur-free carbon tetrachloride mixed with purified hexane or preferably, cyclohexane. Such filters show decomposition after 15 minutes.

The mercury arc has another strong line at 3650A. Filters for isolation of this line have been proposed by Hartmann,[140] Luther and Forbes,[141] Winther,[142] Andrich and Le Blanc,[143] and Buttolph.[144] Absorption data regarding the Luther-Forbes filter (0.78 cm. of a solution containing 0.0785 g. fuchsine S, 0.0164 g. methylene blue, 0.0410 g. *p*-nitrosodimethylaniline per liter) and the Winther filter (1 cm. of 0.03-per cent aqueous Diamant Fuchsine) have been given by Gray.[145] The former gave in a 1-cm. layer a maximum transmission of 8 per cent at 3650A. In one-fifth strength, 2 cm. transmitted 30 per cent. Acids and alkalies alter absorption by the Luther-Forbes filter, as well as that of the Winther filter. It is the opinion of Potapenko [146] that the most suitable form of light filter for Uviol lamps is a stained gelatin film, which may be prepared by coating glass with a gelatin solution containing the desired dye, and after drying, stripping the film so formed. A list of dyes for various wave-lengths was given by Miethe and Stenger [147] and by Mannich.[148] Staats [149] has discussed the problem of making monochromatic glass filters for the wave-lengths 1014, 578, 546, 436, 405, and 365 mμ of the mercury arc. In each, two components are used, (a) a glass which absorbs with sharp cut-off, all radiations of wave-length shorter than the one it is desired to transmit and (b) one with a similar absorption for longer wave-lengths. The ratio of the thicknesses of the two components is specified for each filter. Graphs give the variation in transmission and purity of the transmitted light for each of 15 combinations. In some, auxiliary filters are required. Since the characteristics of such filters depend upon the spectral distribution of the source and the sensitivities of the receivers, they apply only to a specified source (H-3 capillary high-pressure mercury arc) and specified receivers.

[134] Peskov, N. P., *Z. wiss. Phot.*, **18**, 235 (1919); *J. Russ. Phys.-Chem. Soc.*, **47**, 918 (1915).
[135] Oldenberg, O., *Z. Physik*, **29**, 328 (1924).
[136] Coehn, A., and Stuckardt, K., *Z. physik. Chem*, **91**, 722 (1916).
[137] Villars, D. S., *J. Am. Chem. Soc.*, **48**, 1874 (1926).
[138] Taylor, W., *Nature*, **118**, 697 (1926).
[139] Melville, H. W., and Walls, H. J., *Trans. Faraday Soc.*, **29**, 1255 (1933).
[140] Hartmann, J., *Z. wiss. Phot.*, **1**, 259 (1903).
[141] Luther, R., and Forbes, G. S., *J. Am. Chem. Soc.*, **31**, 770 (1909).
[142] Winther, C., *Z. Elektrochem.*, **19**, 389 (1913); for filters for other lines, (5790, 5460, 4360, 4050, and 3130Å), see Winther, C., *Ibid.*, **43**, 691 (1937).
[143] Andrich, K., and Le Blanc, M., *Z. wiss. Phot.*, **15**, 187 (1915).
[144] Buttolph, L. J., *J. Opt. Soc. Am.*, **6**, 1066 (1922).
[145] Gray, L. T. M., *J. Phys. Chem.*, **31**, 1732 (1927).
[146] Potapenko, G., *Z. wiss. Phot.*, **18**, 238; *Chem. Abs.*, **14**, 699 (1920).
[147] Miethe, A., and Stenger, E., *Z. wiss. Phot.*, **19**, 57 (1919); *J. Soc. Chem. Ind.*, **39**, 313A (1920).
[148] Mannich, C., *Chem. Ztg.*, **33**, 1167 (1909).
[149] Staats, E. M., *J. Opt. Soc. Am.*, **28**, 112 (1938).

When it is desired to remove infrared rays to prevent their possible effects on the temperature of solutions undergoing photochemical reactions, water is employed as a filter in a quartz cell. A 1-cm. thickness transmits 58 per cent at 9450A and 14 per cent at 11,900A.[150] Coblentz has suggested filters to absorb the infrared completely.[151] Sodium, potassium, ammonium and thallium chlorides act as selective filters in the region 40-140μ.[152] A filter solution which transmits the visible rays and absorbs ultraviolet rays shorter than about 4000A may be made from quinine sulfate.[153] Clarke [154] describes a light filter for absorbing blue-violet and ultraviolet rays. It is formed of gelatin or other light-transmitting material containing a salt of glucose-phenylosazone-*p,p'*-dicarboxylic acid. An acid which in 0.01 per cent solution (2-cm. layer) absorbs ultraviolet and passes most of the visible rays is made by Suzuki and Sakurai [155] by condensing dextrose or invert sugar with phenylhydrazine-*p*-sulfonic acid in the presence of sodium or potassium acetate at 100°C. Used in a gelatin filter, 2 gms. per sq. meter, this filter completely absorbs the ultraviolet. It is claimed that the insoluble basic lead salt of the acid provides an ultraviolet-ray proof paint. A colorless pyrene compound, such as pyrene-3,5,8,10-tetrasulfonic acid, with steep absorption curve at about 4100A, has been proposed as a filter ingredient for removing ultraviolet rays by Wiegand, Merkel and Tietze.[156] Wilmanns, Dieterle and Weichmann [157] suggest for this purpose cyanines containing two benzoxazole rings, or one such ring and one benzothiazole ring, or a benzoxazole and a thiazoline ring, or a benzothiazole and thiazoline ring, bound in the 2,2'-positions to the nitrogen atom by a carbon atom.

Bakelite panels 0.5 mm. thick transmit 30 per cent at 3126A, 3 per cent at 2800A, and none at 2750A, the resin turning yellow.[158] Zernik [159] proposes hydroxylquinoline sulfonic acids and their alkyl or aryl ethers as colorless light filters for ultraviolet rays.

A filter for wave-lengths between 2900 and 3200A may comprise a film of trihydroxytriethylamine salicylate or *o*-cresotate or other compound of the formula $HO—R—COONH(C_6H_4OH)_3$, where R is a benzene or naphthalene ring and the hydroxyl group of the nucleus and the carboxyl group are in ortho-relation.[160]

A series of long-wave-pass filters has been described by Schneider and Sperti.[161] The shortest mercury arc line which appears on a photospectrogram through 2 cm. of each filter solution following an exposure of 5 seconds (Gaertner quartz spectrograph) is given in Table 16. The line of next shorter wave-length in each case does not appear with an exposure of 60 seconds. The figures given in the second

[150] Nichols, E. F., *Phys. Rev.*, **1**, 13 (1893).
[151] Coblentz, W. W., *Bur. Standards Bull.*, **7**, 655 (1911); **9**, 110 (1913).
[152] Hirsekorn, H. G., *Ann. Physik*, **6**, 985 (1930).
[153] Weyl, Th., "Die Methoden der Organischen Chemie," Vol. **1**, p. 313, Leipzig, G. Thieme, (1909).
[154] Clarke, H. T., U. S. P. 1,293,039, Feb. 4, 1919.
[155] Suzuki, T., and Sakurai, S., U. S. P. 1,684,562, Sept. 18, 1932, to Zaidan Hojin Rikagaku Kenkyujo; *Chem. Abs.*, **22**, 4735 (1928). British P. 242,721, Aug. 18, 1924.
[156] Wiegand, C., Merkel, E., and Tietze, E., U. S. P. 2,122,828, July 5, 1938; *Chem. Abs.*, **32**, 6509 (1938).
[157] Wilmanns, G., Dieterle, W., and Weichmann, H. K., German P. 654,900, Jan. 4, 1938; *Chem. Abs.*, **32**, 3268 (1938).
[158] Risler, J., *Compt. rend.*, **181**, 782 (1925).
[159] Zernik, F., U. S. P. 1,688,259. Oct. 16, 1928; *Brit. Chem. Abs.*, **B**, 528 (1929).
[160] Stockelbach, F. E., U. S. P. 2,128,334, Aug. 30, 1938; *Chem. Abs.*, **32**, 8274 (1938).
[161] Schneider, H., and Sperti, G., *Bull. Basic Sci. Research*, **1**, 9 (1926); Goode, G. P., *Ibid.*, **5**, 41 (1933).

column are the number of cubic centimeters of water in which one gram of substance is dissolved.

Table 16.—Transmission of Ultraviolet Rays by Filters.

Salt	Dilution	Wave-length Limit, A
Ammonium Sulfate	Concentrated	2030
Strontium Chloride	Concentrated	2120
Calcium Chloride	2	2220
Acetic Acid	500	2250
	50	2300
	20	2370
Lead Acetate	(0.28 g. per l.)	2380
	1000	2450
	600	2480
	200	2570
Copper Sulfate	100	2570
Lead Acetate	(15 g. per l.)	2650
	40	2680
	20	2750
Copper Sulfate	40	2880
	25	2960
	3	3130
Cupric Chloride	20	3340

In the preparation of these filters, no attention was paid to the purity or hydration of the materials. Instead, after preparation, the filters were tested spectrographically and adjusted by the addition of water or concentrated salt solution. A semi-commercial scale apparatus in which these filters may be employed for the irradiation of large areas of solutions or liquids of various kinds has been described. (Figure 91.)[162]

Two Hanovia 500-watt quartz mercury arc burners, operated at 135-145 volts a.c. are housed in two separate square metal shields equipped with air-cooling louvres. On the housing of each burner are mounted three filter cells, the frames of which are of chromium-plated brass, 10 by 17.5 cm., equipped with large quartz filter plates 2 cm. apart. The quartz plates are sealed to the cell frames with picein wax. The joints on the side next to the lamp are cooled by water which flows through the hollow section of the filter frame. The filter solutions are kept in five-gallon glass storage bottles in the top of the unit. All piping and valves in the filter feed and drain lines are either copper, brass, or chromium-plated brass. The filter solutions are forced through the lines by air pressure, maintained at ten pounds by a regulator. The flow is made visible by a drip cup in the drain line mounted on the front of the unit; its rate is adjusted to change the solution in each cell every fifteen minutes. Six different filter solutions and distilled water are available for each lamp at any time by opening the proper line valves on the front panel. Nitrogen and ice water outlets are mounted on the unit so that a nitrogen atmosphere and cooling may be applied continuously to the material irradiated. Motor-driven rotating and stirring devices are built into each lamp housing. It is possible to irradiate oils in thin films in large rotating cylinders, solutions in rotating test tubes, and liquids in various types of cells equipped with stirrers. The distance from the burners to the cells is approximately 15 cm. Three experiments, utilizing different filters, may be carried on simultaneously with each lamp, or six with the complete unit.

Withrow[163] describes filters for the region 2900 to 3200A, made of solutions of organic acids adsorbed on regenerated cellulose or impregnated in gelatin sheets, the latter being the stronger and having the smoother surfaces. In each of the

[162] Goode, G. P., *Bull. Basic Sci. Research,* **5**, 39 (1933); U. S. P. 1,966,546-7, July 17, 1934, to General Development Laboratories, Inc.

[163] Withrow, R., *Bull. Basic Sci. Research,* **3**, 82 (1931); U. S. P. 1,938,734, Dec. 12, 1933, to General Development Laboratories, Inc.

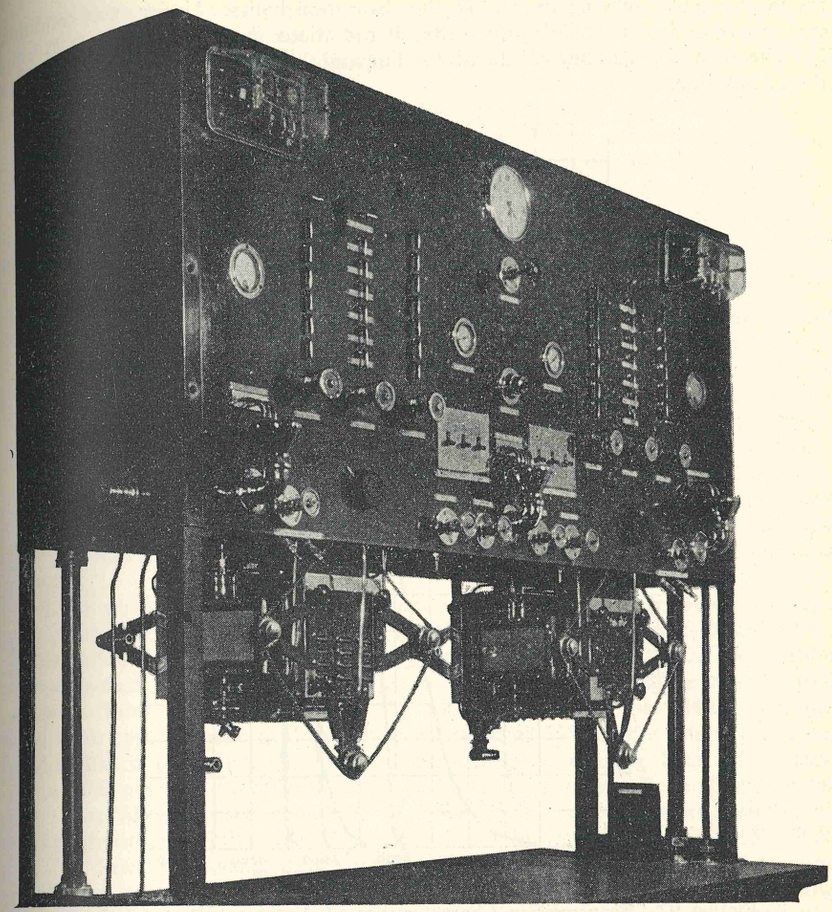


FIGURE 91. Ultraviolet Irradiation Unit. (Goode, *Bulletin Basic Science Research*).

three solutions used, the solvent is one liter of water and 125 cc. of glycerin to prevent cracking. No. 1 contains 80 gm. of sodium benzoate, No. 2, 40 gm. of potassium acid phthalate[164] and No. 3, 30 gm. of cinnamic acid and 10 gm. of potassium hydroxide. Sheets of the desired size of No. 600 Du Pont Cellophane are soaked in the desired solution for 12 hours and allowed to dry. In making gelatin filters, powdered gelatin in unspecified quantity is dissolved in the filter solution and the liquid spread on sheets of glass or quartz. The transmission curves of these three filters are given in Figure 92, in which Corex D and Quartz-lite are added for comparison. On intense irradiation, particularly with the shorter wave-lengths, these filters deteriorate, the absorption limit shifting toward longer wave-lengths. For this reason, it is advisable to use these filters in conjunction with a filter of Corex D which absorbs much of the energy in the shorter wave-lengths,

[164] Suggested by Saunders, F., *J. Opt. Soc. Am.,* **16**, 362 (1928).

the gelatin filters serving to sharpen the absorption limits. Under such conditions, two sheets of No. 1, absorb practically all radiations shorter than the 2890A line, two sheets of No. 2 all beyond the 3130A line and three sheets of No. 3 those beyond the 3340A line.

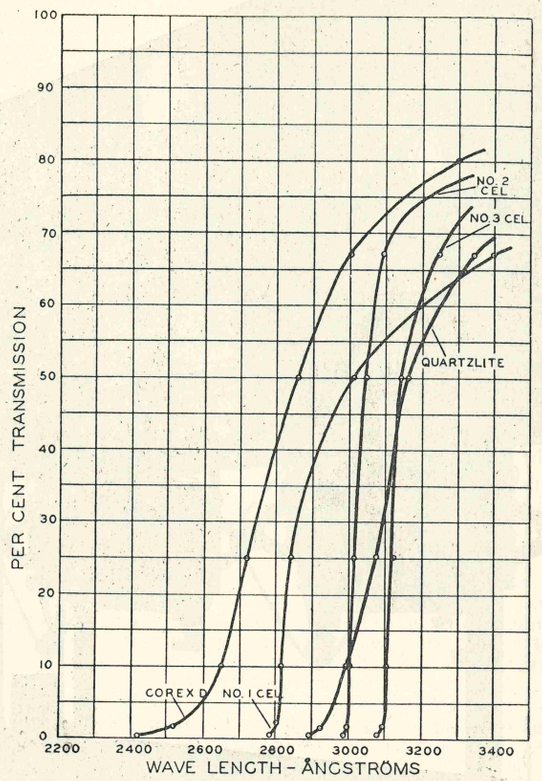


FIGURE 92. Transmission Characteristics of Various Filters (Withrow, *Bull. Basic Science Research*).

Jones [165] described a set of eight filters, only two of which were intended for the ultraviolet region, the others covering the visible and infrared. One ultraviolet filter was made by combining 2 cm. of 10 per cent copper sulfate solution with 3.2 mm. of Corning glass G 586. This filter transmits between 3300 and 4300A with a maximum of 69 per cent at 3800A. At all wave-lengths between 4300 and 12,000A, transmission is less than 0.1 per cent. The other ultraviolet filter combined a 1 cm. layer of a 50 per cent aqueous solution of $NiSO_4.7H_2O$ with 3.2 mm. of Corning glass G 986A. It transmits between 2600 and 3600A, with a maximum of 50 per cent at 3100A. By adding 1 cm. of 2 per cent $CuSO_4.5H_2O$, all wave-lengths shorter than 3100A can be absorbed. Bhagwat [166] has determined the transmission of solutions of nickel salts. Combinations of these salts with cobalt salts transmit only in the ultraviolet, a mixture of 3.66*M* cobalt chloride and 2.08*M* nickel nitrate transmitting 3307-3598A. The cobalt salt alone transmits the 2618-4063 and 7100-7600A regions.

[165] Jones, L. A., *J. Opt. Soc. Am.*, **16**, 259 (1928); *J. Nutrition*, **2**, 111 (1929); *Chem. Abs.*, **24**, 1889 (1930).

[166] Bhagwat, W. V., *J. Indian Chem. Soc.*, **11**, 5 (1934); *Bull. Acad. Sci. United Provinces Agra Oudh*, **2**, 67 (1932); *Chem. Abs.*, **29**, 7192 (1935).

Another list of ultraviolet filters for the mercury lamp, most of which also remove the infrared, has been proposed by Bowen,[167] who employs the filters in round flasks which serve as condensers, increasing the light intensity. One flask a few centimeters from the lamp gives approximately parallel light. Two flasks almost in contact and with one nearly touching the burner, give more intense light converging to an image about 5 cm. beyond the second flask. For the regions (a) the yellow and green lines and (b) blue, violet and 3665A lines, the first flask (glass, 10-12 cm. diameter) contains distilled water and the second, a double-walled Dewar flask, has the inner part filled with water and the 1-cm. space filled with a solution of 60 gm. $CuSO_4 \cdot 5H_2O$, 2 gm. $K_2Cr_2O_7$, 55 cc. of concentrated sulfuric acid and made up to one liter with water. With this arrangement, 3.4 mm. Corning 344 transmits only the 5790 and 5770A lines, and 5 mm. Corning 512 only the green line 5460A. For the region (b), the solution for the outer part of the Dewar flask is 20 gm. $CuSO_4 \cdot 5H_2O$ and 300 cc. aqueous ammonia made to one liter with water. With this solution, 2.5 mm. Corning Noviol A glass transmits only the blue line 4360A, 2 mm. of Corning Noviol 0 and 1 cm. of a carbon tetrachloride solution of iodine (7.5 gm. per liter) transmits only the 4060A line and 2 to 2.5 mm. of Chance's black ultraviolet glass transmits only the line 3665A.

For the ultraviolet region, 10 cm. spherical quartz flasks are used. For the region 3340-2800A, the first flask has a solution of 70 gm. $NiCl_2 \cdot 6H_2O$ and 30 cc. concentrated hydrochloric acid per liter. For the region 2800-2480A, a solution of one-fifth that concentration is employed. These solutions remove the infrared and 4060A lines and greatly reduce the 3665A line. For the 3340A line, the second flask contains uric acid in water saturated at 15°C. For the 3135A line, this flask has a potassium chromate solution made by diluting 5 cc. of a stock solution (3.0 gm. per liter) with 5 cc. of 2*N* sodium hydroxide and 490 cc. of water. The filter is used with a 1-cm. plane quartz cell containing circulated potassium hydrogen phthalate (13 gm. per liter) in water. For the 3135, 3030 and 2970A lines, the second flask contains 60 cc. of a stock solution of Auramine 0 (0.125 gm. per liter) in 440 cc. of water, and is used with 1 cm. of circulating saturated benzoic acid in water. For the 3030 lines (and all shorter ones), the second flask contains water. For the 3030A line, there is used 1 cm. of benzene circulating at the rate of 4 liters per hour; for 2650A, chlorine gas at 760 mm. (3 cm. layer) and a circulating solution of pure benzene in water (1 cm.) (82 cc. of the saturated solution at 15°C. diluted to 100cc.). For the 2750-2480A lines, 3 cm. of chlorine gas at atmospheric pressure is used. For the 2540A line, there is employed in addition to the chlorine filter, 1 cm. of a solution made by diluting 8.6 cc. of a solution of 12.7 gm. iodine and 18 gm. of potassium iodide per liter, to one liter. Transmission data for these filter arrangements are given. Some changes in the list were made subsequently.[168]

Slightly different filters, employing also cobalt sulfate in sodium cinnamate, have been recommended by Bäckström [169] for the medium ultraviolet region. Another series, using cobalt, chromium, copper, manganese and nickel salts has

[167] Bowen, E. J., *J. Chem. Soc.*, 2236 (1932).

[168] Bowen, E. J., *J. Chem. Soc.*, 76 (1935).

[169] Bäckström, H., *Naturwiss.*, **21**, 251 (1933).

been described by Maddock [170] for isolating nine of the principal bands of the mercury spectrum from 2652 to 5780A, giving transmissions of 7 to 36 per cent. Still others are due to Vaidya,[171] who describes 33 such systems and gives approximate measurements of the energy transmitted by eight of them.

For isolating for Raman studies the mercury triplet at 4358A, Sannié, Amy and Poremski [172] use a filter solution containing 5 per cent nitrobenzene and 0.01 per cent rhodamine 5G Extra in ethanol. A thickness of 1 cm. gives a transmission of 0.001 for the lines 4046 and 4916 and of 0.95 for the desired triplet. Glass filters for other lines for Raman work have also been described by Amy.[173]

In Raman work, the 4046A line is better absorbed by Noviol A than by sodium nitrite solution, which is subject to change.[174]

According to Bhagwat and Dhar [175] the ammonia complex of cupric chloride is a good filter for the region 4000 to 4590A. Cupric chloride with cobaltous chloride is satisfactory for the lines 2961 and 3248-74A.

Mica [176] has occasionally been used as a filter material. Ruby mica absorbs the least; in a 0.03 mm. layer the transparency limit is 2900A. In 0.75 mm., it is 3500A. Green species absorb more strongly, as only traces pass through 0.5 mm. layers. Deep-brown Madagascar mica absorbs totally in 0.1 mm. layers.[177]

Transmission by Clothing. It is of interest to consider the degree to which our clothing prevents access of the ultraviolet to the body. Dozier and Morgan [178] were unable to produce vitamin D in oils by irradiating them through baby flannel, pongee and crepe de Chine, although artificial silk and meadow lane materials transmitted the active rays. The mean interspace between threads and the weight are the important factors.[179] Trotman,[180] who used a light sensitive dyestuff as an indicator of the permeability of the fabric to ultraviolet, was unable to detect any transmission even through viscose, cuprammonium, chardonnet and celanese rayons. Coblentz, Stair and Schoffstall [181] have made physical measurements of the transmission of ultraviolet radiation through various fabrics. Comparing materials having the same weight, practically no difference was found in the amount transmitted through bleached samples of cotton, linen, viscose silk and cellulose acetate silk. Fresh, white natural silk is almost as translucent as bleached cotton, but wool is only half as transparent. In all cases when the fabric is dyed, or slightly yellow with age, the ultraviolet transmission through the thread is greatly decreased. Hence, in comparing dyed fabrics, the one with the largest openings between the threads transmits the most ultraviolet radiation.

Hirst, King and Lambert [182] found every one of over a hundred fabrics to cut off a large proportion of the ultraviolet radiation, the weave and texture being more important than the material of the fiber. For equal thicknesses of material,

[170] Maddock, A. J., *J. Sci. Instruments*, **12**, 218 (1935).
[171] Vaidya, B. K., *J. Univ. Bombay*, **3**, Pt. 2, 141 (1934); *Chem. Abs.*, **29**, 6508 (1935).
[172] Sannié, C., Amy, L., and Poremski, V., *Compt. rend.*, **202**, 1042 (1936).
[173] Amy, L., *Documentat. Sci.*, **4**, 97 (1935); *Chem. Zentr.*, **II**, 2848 (1935).
[174] Biquard, D., *Documentat. Sci.*, **5**, 81 (1936); *Chem. Abs.*, **31**, 7758 (1937). See, however, Bayley, P. L., *J. Opt. Soc. Am.*, **27**, 303 (1937).
[175] Bhagwat, W. V., and Dhar, N. R., *J. Phys. Chem.*, **35**, 2383, 2391, 2401 (1931).
[176] Hausmann, W., and Krumpell, O., *Strahlentherapie*, **35**, 387 (1930); Takagi, T., *Ibid.*, **40**, 189 (1931).
[177] Finkelnburg, W., *Naturwiss*, **14**, 919 (1926).
[178] Dozier, C. C., and Morgan, H., *Am. J. Physiol.*, **84**, 603 (1928).
[179] Morgan, H., *Am. J. Physiol.*, **86**, 32 (1928).
[180] Trotman, S. R., *Textile Recorder*, **47**, 63 (1929); *Chem. Abs.*, **23**, 2297 (1929).
[181] Coblentz, W. W., Stair, R., and Schoffstall, C. W., *Bur. Standards J. Research*, **1**, 105 (1928).
[182] Hirst, H. R., King, P. E., and Lambert, P. N., *J. Soc. Dyers Colourists*, **44**, 109 (1928); *Chem. Abs.*, **22**, 2061 (1928); Eccles, J., *Silk J.*, **7**, 37 (1931).

they believed wool to have on the whole a higher transmissive power than the other fabrics tested. Any kind of dyeing decreases the ultraviolet transmission.

Young [183] suggested tracing cloth as a substitute for the more expensive ultraviolet glasses for use in country cottages, chicken farms, etc. This could not be confirmed at the Bureau of Standards. The total ultraviolet of wavelengths 2500-3100 diffusely transmitted through a new sample of tracing cloth amounted to about 26 per cent before wetting and 14 per cent after removing the sizing and drying the cloth. Balloon fabric transmits 21, batiste 16, and nainsook 31 per cent.

Physical Methods for Isolating Lines or Wave-Length Bands

Unique among filters employing physical principles is that of Christiansen, which acts on [184] the principle that a suspension of a finely divided solid in a liquid transmits only radiations of the wave-length at which the refractive index of the solid is the same as that of the liquid. While such filters have frequently been used in the visible region, the principle has only recently been extended to the ultraviolet.[185] A solution of 56 per cent benzene and 44 per cent ethanol containing amorphous silica at 20°C. transmits at 3600A. Such filters are very sensitive to temperature changes. Andrews [186] furnishes details of an apparatus for separating visible from ultraviolet light, which depends upon the fact that the visible rays are less refracted by a lens than is the ultraviolet radiation. Figure 93 diagrammatically shows the design of the apparatus. A is a source of visible

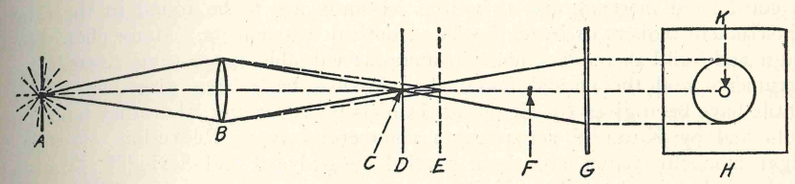


Figure 93. Diagram Showing Principle of Andrew's Separator.

light, also producing ultraviolet rays. B is a quartz lens. D is a thin sheet of metal pierced with a pinhole at C, the diaphragm being so placed that the pinhole is in the exact mean focus of the visible rays. F is a small metal disk and G is a screen. A front view of the screen is shown at H. The operation of this instrument is based on the fact that the mean focus of the visible light is located at a measurable distance beyond the mean focus of the invisible rays owing to the greater refrangibility of the latter over that of the former. If, therefore, the diaphragm D is carefully adjusted so as to bring the pinhole C into the exact mean focus of the ultraviolet rays, the rays of the latter will pass through the pinhole and spread out again on the other side of the diaphragm. The mean focus of the visible light being some distance beyond the pinhole, its rays will be largely intercepted by the diaphragm, and through the pinhole only a few of the nearly parallel rays of visible light will pass. In operation, if the screen H is made of non-fluorescent material, there will appear on it only the small illumi-

[183] Young, C. H., *Nature*, **123**, 47 (1929).
[184] See Holst, G., *Z. wiss. Phot.*, **36**, 145 (1937); *Brit. Chem. Abs.*, **B**, 479 (1937).
[185] Kohn, H., and v. Fragstein, K., *Physik. Z.*, **33**, 929 (1932); Ahier, G., *Compt. rend.*, **205**, 37 (1937).
[186] Andrews, W. S., *Gen. Electric Review*, 817 (1917).

nated spot K, but if it be coated with a fluorescent substance, such as powdered willemite, this small luminous spot will be surrounded by a disk of bright green light produced by the fluorescence of the willemite excited by the circular field of invisible ultraviolet rays. Should it be found desirable to cut out the spot of visible light, the small metal disk F can be set up in such a position as to cast its shadow over the spot K and so transform it from a bright spot to a dark one, leaving the disk of green fluorescent light otherwise unchanged.

The method has been extended by Terenin[187] to the separation of various ultraviolet regions. Forbes, Heidt and Spooner[188] prefer it to the monochromator for the aluminum lines around 1940A and the zinc lines near 2030-2014A.

Another way of getting a monochromatic radiation is to employ the rays given out by cold mercury vapor when transversely illuminated by a mercury vapor arc. This radiation is about one-fortieth as intense as the 2537A line of the original source, but offers some possibilities for photochemical work.[189] Very low voltage arcs also deliver monochromatic radiation in the resonance lines, but this radiation is of low intensity.[190]

By far the most generally used optical method employs a prism monochromator. Light from the source passes through a slit to a prism (a collimating lens may be added) and after passing a lens emerges through an exit slit, which is narrow enough to exclude all but the desired wave-length region. This slit is also movable so that any desired wave-length range may be isolated. Any such instrument must, however, represent a compromise between monochromatic purity and loss of intensity. For greater intensities, monochromators are best employed with the constricted mercury arc as source. Details are to be found in the catalogs of instrument makers or in textbooks on optical instruments. Many photochemists design and build their own monochromators; valuable suggestions regarding such instruments and the optical losses they involve have been given by Forbes.[191] Details have been given by Heidt and Daniels[192] regarding laboratory-built instruments and by Kurtz[193] regarding a commercial type. Reflection losses in the Hilger monochromator have been studied by Ridyard and Style.[194] Granath[195] calculates that in the Hilger E 31 quartz spectrograph, the absorption at 1860A by the quartz is 50 per cent and by the air 17 per cent. At 1900A, the values are 31 per cent and 3 per cent, at 2000A, 23 per cent and 1 per cent and at 2100A, 16 per cent and 0.5 per cent, respectively. Forsythe and Barnes[196] have described a quartz monochromator especially intended for studying the intensity of the radiation in the ultraviolet spectrum from various sources.[197]

[187] Terenin, A., *Z. Physik*, **31**, 33 (1925).

[188] Forbes, G. S., Heidt, L. J., and Spooner, L. W., *Rev. Sci. Instruments*, **5**, 253 (1934).

[189] Wood, R. W., *Physik. Z.*, **13**, 353 (1912); Cario, G., and Franck, J., *Z. Physik*, **17**, 205 (1923).

[190] Foote, P. D., and Meggers, W. F., *Bur. Standards Bull.*, **16**, 317 (1920).

[191] Forbes, G. S., *J. Phys. Chem.*, **32**, 496 (1928).

[192] Heidt, L. J., and Daniels, F., *J. Am. Chem. Soc.*, **54**, 2384 (1932); see also Benford, F., *J. Opt. Soc. Am.*, **26**, 99 (1936).

[193] Kurtz, H. F., *J. Opt. Soc. Am.*, **13**, 495 (1926); see also Villars, D. S., *J. Am. Chem. Soc.*, **49**, 326 (1927).

[194] Ridyard, H. N., and Style, D. W. G., *J. Phys. Chem.*, **32**, 861 (1928).

[195] Granath, L. P., *Phys. Rev.*, **34**, 1045 (1929).

[196] Forsythe, W. E., and Barnes, B. T., *Rev. Sci. Instruments*, **1**, 569 (1930).

[197] See also Fortrat, R., *Rev. optique*, **16**, 386 (1937); Pelton, M. O., *J. Sci. Instruments*, **15**, 169 (1938); Perry, J. W., *Proc. Phys. Soc.* (London), **50**, 265 (1938).

Chapter 11

The Sun as a Source of Ultraviolet Radiations

The discussion of filters in the preceding chapter paves the way for a consideration of the amount and quality of the ultraviolet energy available on the earth's surface, since a large portion of the energy emitted by the sun is absorbed in the earth's atmosphere. Only about 70 to 78 per cent of the sun's total radiant energy of all wave-lengths which strikes the upper atmosphere gets through to sea level when the sun is at the zenith and the air is free from dust and clouds.[1]

Astrophysical evidence indicates that the past billion years is only a small fraction of the period since the sun began to shine. In the past billion years, it has emitted 1.20×10^{50} ergs of energy (3.79×10^{33} ergs per second times 10^7 seconds per year $\times 10^9$ years). This is more than three billion billion billion billion kilowatt-hours. Expressed per gram of the sun's mass (1.983×10^{33} grams), the radiation per year is 6.05×10^7 ergs (1.44 calories); in a billion years at this rate, the radiation has amounted to 6.05×10^{16} ergs per gram, a lower limit.

It is believed that the whole ball of the sun is composed of hot gases, increasing inward in temperature and density. We see only the surface layer of gases—only down to where the density is a thousandth part of an atmosphere. This visible skin—photosphere—contains only as much mass as would a layer of a few feet of atmospheric air around the sun, far too little to produce the intense energy radiation. This must, therefore, be produced below the photosphere and flow toward the surface, which itself has a temperature of about 6000°K.

Many suggestions have been made as to the nature of the processes producing this energy; most of those based upon processes experimentally familiar have been found quantitatively inadequate. Recently, astronomers such as Eddington, have adopted the principle of Einstein that mass is in some way equivalent to energy and have built upon this models to describe the solar, or more generally, stellar radiation processes.

This principle states that a loss of m units of mass corresponds to the liberation of mc^2 units of energy, where c is the velocity of light. This constitutional energy is 8.99×10^{20} ergs per gram, about 15,000 times the estimated radiation per gram of the sun's mass during the past billion years. The Einstein principle of the equivalence of energy and mass would imply that the sun is losing 4,660,000 tons as energy per second, the earth receiving four pounds and three ounces as energy per second.[2]

In Eddington's theory, the material throughout the sun is in the state of a nearly perfect gas, the density increasing toward the center at such a rate that at the center it is about 54 times the mean density (1.41 grams per cubic centi-

[1] Stewart, J. Q., [*J. Frank. Inst.*, **204**, 438 (1927)] has given an interesting general account of the theories of the origin of stellar energy, from which much of the information in these paragraphs has been derived.

[2] Discussion by Eddington, A. S., *Nature*, **117**, Supplement to May 1 (1926); see, however, Jeans, Sir J., *Nature*, **117**, 689 (1926); Menzel, D. H., *Science*, **65**, 431 (1927); Nernst, W., *J. Frank. Inst.*, **206**, 135 (1928). See also, Landau, L., *Compt. rend. acad. sci. U.R.S.S.*, **17**, 305 (1937); *Chem. Abs.*, **32**, 2426 (1938).

meter). This would make the central density more than three times greater than that of platinum. The gas at the center of the model sun is assumed to be under a pressure of more than a billion atmospheres and at a temperature of nearly 40 million degrees K. At such temperatures, it is believed that the shells of electrons are torn off from the atoms, leaving them stripped so that the kernels which remain are small enough for the gas to behave as such despite its high density.

Although considerations such as these are highly speculative, they may serve to afford some conception of the nature of the problems involved.

In the spectra of the sun about 60 elements have been identified.[3] Russell[4] has surveyed and discussed the evidence regarding the relative abundance of the elements in the sun's atmosphere. Sodium, magnesium, silicon, potassium, calcium and iron form 95 per cent of the whole mass. Elements of even atomic numbers are ten times as abundant as those of odd atomic numbers. The metals from sodium to zinc are far more common than any others. Compounds are present only in small amounts, cyanogen being rarer than scandium. The presence of boron and phosphorus has been much discussed. The estimated temperature of the reversing layer is 5600° and the pressure at its base is 0.005 atmosphere. It appears to contain 60 parts of hydrogen (by volume), two of helium, two of oxygen, one part of metallic vapor and 0.8 of free electrons. The temperature of the sun spots is close to 4900° absolute.[5]

Effects of the Earth's Atmosphere on Solar Radiation. Most of the lines which have been studied in deriving information on solar radiation have been located in the infrared and visible regions. Only a small part of the ultraviolet adjacent to the visible has been included. This is because the earth's atmosphere absorbs the shorter ultraviolet radiations; according to Lyman, the physicist Cornu found the spectrum of the sun to terminate quite abruptly at about 3000A. Our knowledge of the actual ultraviolet output of the sun, or of the amount of ultraviolet energy which reaches the outer layers of the earth's atmosphere is, therefore, limited because of absorption of ultraviolet within the atmosphere. It has been necessary to depend upon indirect methods, such as a consideration of the nature of the absorbing substance or substances and their distribution in the atmosphere in drawing conclusions as to the probable amounts of ultraviolet reaching the outer atmosphere. The most extensive estimates of the energy distribution outside the atmosphere have been made by Abbot[6] for the region 4000A, and by Fabry and Buisson for shorter wave-lengths.[7] The way in which this energy distribution is computed is about as follows: A series of observations is made of the normal incident energy at various times throughout the day. At these different times the rays pass through different lengths (or masses) of atmosphere. A vertical path gives an "air mass" of one. For variations from the vertical, the "air mass" varies as the secant of the angle. By graphical methods, it is possible to obtain from a series of intensity observations with different "air masses" an extrapolated value for an "air mass" of zero which represents the sun's energy before it is filtered by the atmosphere. Thus at 3100A the transmission for "air mass" of 1 is 0.1, and for "air mass" of 2, 0.01 (8 A.M. or 4 P.M.) and at "air

[3] St. John, C. E., *Proc. Nat. Acad. Sci.*, **15**, 789 (1929); *Astrophys. J.*, **70**, 160 (1930); Dingle, H., in article "Sun" in *Encyclopedia Brittanica*, 14th ed.

[4] Russell, H. N., *Astrophys. J.*, **70**, 11 (1929).

[5] Richardson, R. S., *Astrophys. J.*, **73**, 216 (1931).

[6] Abbot, C. G., *Smithsonian Miscellaneous Collections*, **74**, 15 (1923); *Annals Astrophysical Observatory*, **2**, 112 (1908).

[7] Fabry, C., and Buisson, H., *Compt. rend.*, **175**, 156 (1922); *Astrophys. J.*, **54**, 297 (1921).

mass" of 3 it is only one part in a thousand.[8] During the stratosphere flight of the Explorer II to 72,395 feet, the total ultraviolet increased not over 4 per cent.[9]

From the standpoint of the biologist, the absorption of radiations of the shorter ultraviolet rays by the atmosphere is of the greatest importance. It is shown in Chapter 35 that ultraviolet rays shorter than about 2950A are lethal to bacteria and destructive to living cells. Life, as we know it, could not exist on the earth if the absorption of these shorter rays in the atmosphere did not occur.

It is, therefore, interesting to determine which component of the atmosphere absorbs these rays. Both oxygen and nitrogen absorb strongly only rays of very much shorter wave-length (1850A and less than 1250A, respectively). Accurate data on the absorption by oxygen in the region 1850 to 2300A have been determined by Granath.[10] Earlier important observations were due to Fabry and Buisson,[11] Ladenburg and Lehmann,[12] and Hallwachs.[13] That the absorbing component for bactericidal radiations is ozone has been known for many years, Hartley having been credited with first suggesting it.[14] The origin of ozone in the upper atmosphere is still, however, an unsolved problem, despite a considerable amount of work.[15] According to Fabry,[16] a thickness of ozone of about 3 mm. at normal temperature and pressure would account for the observed absorption. This was calculated from absorption measurements of known concentrations of ozone and of varying thicknesses of the absorbing layer of the earth's atmosphere. Subsequently, a number of papers have been devoted to the distribution of ozone in the atmosphere.

Probably the best opportunity for accurate studies was afforded by the stratosphere flights of the Explorers I and II. These indicated little ozone up to 52,000 feet. Above this, the concentration of ozone increased rather rapidly and at 72,000 feet nearly 25 per cent of the total quantity of ozone lay below the level of the balloon. In the summer flight of 1934, the ozone was equivalent to 2.5 mm. and in the November flight of 1935 to 1.9 mm.[17]

Nitric acid occurs in the atmosphere, more at high than at low altitudes.[18] It has been suggested that the nitrates and nitrites present in the atmosphere are derived from the photochemical oxidation of ammonia.[19] Vorländer and Gohdes[20] find moist air to contain oxides of nitrogen to the extent of $15\text{-}30 \times 10^{-6}$ gm. per

[8] Gordon, N. T., and Benford, F., *Gen. Electric Review*, **33**, 283 (1930).

[9] Teele, R. P., *National Geographic Society, Stratosphere Series*, No. 2, 133 (1936).

[10] Granath, L. P., *Phys. Rev.*, **34**, 1045 (1929).

[11] Fabry, C., and Buisson, H., *Compt. rend.*, **156**, 782 (1913).

[12] Ladenburg, E., and Lehmann, E., *Ber. deutsche physik. Ges.*, **4**, 125 (1906).

[13] Hallwachs, W., *Ann. Physik*, **30**, 602 (1909).

[14] Hartley, W. N., *J. Chem. Phys.*, 111 (1881), cited by O'Brien, B., *National Geographic Society, Stratosphere Series*, No. 2, 49 (1936). For recent observations, Dejardin, G., and Arnulf, A., *Compt. rend.*, **205**, 1000 (1937); Vassy, E., *Ann. phys.*, **8**, 679 (1937).

[15] Rayleigh, Lord, *Science*, **70**, 83 (1929); Rosseland, S., *Nature*, **123**, 761 (1929); Ångström, A., *Gerland's Beitr. z. Geophysik*, **21**, 2, 145 (1929); Dobson, G. M. B., Harrison, D. N., and Lawrence, J., *Proc. Roy. Soc.*, **114A**, 521 (1927); Dauvillier, A., *Compt. rend.* **197**, 1339 (1933); Barbier, D., Chalonge, D., and Vassy, E., *Compt. rend.*, **201**, 787 (1935); Fowle, F. E., *J. Terrestrial Magnetism and Atm. Elec.*, **33**, 151 (1928); Dobson, G. M. B., Kimball, H., and Kidson, E., *Proc. Roy. Soc.*, **129A**, 411 (1930); Wulf, O. R., *Phil. Mag.*, **17**, 251 (1934); *J. Opt. Soc. Am.*, **25**, 231 (1935); Harteck, P., *Naturwiss.*, **19**, 858 (1931); Mecke, R., *Z. physik. Chem. Bodenstein Festschrift*, 329 (1931); Saha, M. N., *Proc. Roy. Soc.* **A160**, 155 (1937).

[16] Fabry, C., *J. Math. Physics*, **4**, 1 (1925); Cabannes, J., and Dufay, J., *J. Phys. Radium*, **7**, 257 (1926).

[17] O'Brien, B., *National Geographic Society, Stratosphere Series*, No. 2 (1936). Compare Regener, V. H., *Z. Physik*, **109**, 642 (1938). A recent theoretical calculation of the vertical distribution of ozone is due to Wulf, O. R., and Deming, L. S., *Terr. Mag.*, **41**, 299 (1936).

[18] Rao, G. G., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **199**, 422 (1931).

[19] Rao, G. G., *Bull. Acad. Sci., United Provinces Agra Oudh Allahabad, India*, **1**, 82 (1931); *Chem. Abs.*, **26**, 5849 (1932).

[20] Vorländer, D., and Gohdes, W., *Ber.*, **64B**, 1776 (1931).

cubic meter of N_2O_3. Irradiation with ultraviolet increases this from ten to a hundred times. Ammonia may be decomposed into nitrogen and hydrogen in the stratosphere.[21] Formaldehyde may also be present in air since it may be detected in rainwater. The amount therein is not increased by lightning, but is greater when the rainfall has been preceded by some sunny days. Dhar and Ram [22] suggest that formaldehyde may be produced from carbon dioxide and water by radiation of wave-length 2550A, at altitudes where this radiation has not all been absorbed by the ozone layer.

Suspended ultramicroscopic particles, partly consisting of ammonium nitrite and nitrate and sodium chloride and perchlorate, cause a scattering of radiations, greater at altitudes above those where rain exerts a cleansing effect. Duclaux [23] believes that this may play some part in causing the disappearance of the solar spectrum beyond the ozone bands, and that absorption by oxygen in the short wave region may not wholly account for it.

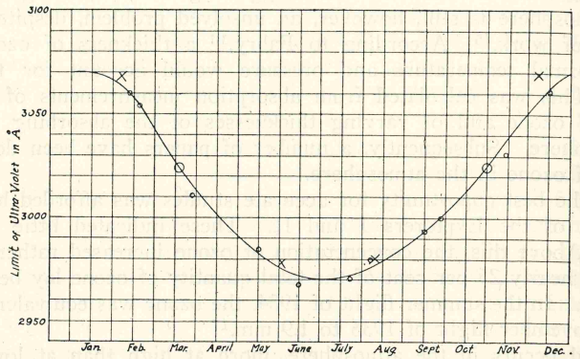


FIGURE 94. Prof. Winchester's Limit of Blackening on Photographic Plates for North Sky at New Brunswick (N. J.) for Different Seasons of the Year (Forsythe and Christison, *General Electric Review*). The vertical line above each month denotes its beginning. ○ = Winchester's values. × = Points plotted from data in paper of Forsythe and Christison. ⊙ = Two calculated points.

Limits of the Solar Spectrum. Comparatively few workers have been interested in determining the long wave region at which solar radiation first penetrates to the earth. Adel, Slipher and Barker [24] place it at 13.5μ and attribute it mainly to vibration spectra of carbon dioxide and to a lesser extent to ozone. Beyond 17μ there is also absorption by water vapor, the effect of which is also observed in the red region of the visible, according to Beletskii.[25] The regions 8-9 and 10-12μ have high transparency. This radiation in the remote infrared is, however, insignificant in amount; Coblentz and Kahler [26] have stated that but little radiation of wave-lengths greater than 2μ is transmitted by the earth's atmosphere. On some days the infrared energy component from about 2 to 3μ to the limit of the visible may be larger than the visible component. On clear days the two components may be about equal or the visible one may exceed the infrared.

[21] Matignon, C., *Chimie et Industrie,* Special No. 328, September, 1925.
[22] Dhar, N. R., and Ram, A., *Nature,* **132,** 819 (1933).
[23] Duclaux, J., *J. phys. Radium,* **4,** 625 (1933).
[24] Adel, A., Slipher, V. M., and Barker, E. F., *Phys. Rev.,* **47,** 251, 580 (1935).
[25] Beletskii, F. A., *Zhur. Geofiz.,* **6,** 64 (1936); *Chem. Abs.,* **31,** 3383 (1937).

There have been many determinations of the short-wave length limit since the time of Cornu, but his value of 3000A holds fairly well. The exact value varies greatly with seasonal, altitudinal and other influences. Coblentz and Kahler believed that radiations less than 3000A, if present, amount to less than 5 per cent (20 per cent in the mercury arc) of the total ultraviolet component. Others have stated the limit as 2900A or 2845A. Its variation at Davos in the Swiss Alps has been widely quoted.[27] From December to February, it was 3120A, September to November, 3080A, March to May, 3010A, June to August, 2962A.[28] Fabry and Buisson [29] showed that the amount of energy of wave-length 2900A that reaches the earth's surface is only one-millionth that for 3140A, and even for the larger value the intensity is small. Winchester has given an experimental curve (Figure 94) showing the wave-length limit at New Brunswick, N. J., as detected by the blackening of photographic plates exposed to the north sky at various times of the year. The shortest wave-length found was 2968A on June 1.[30]

Amounts and Distribution of Solar Ultraviolet

Coblentz and Kahler [31] state that the maximum normal solar radiation at perpendicular incidence varies from 1.37 gram calories per minute per square centimeter in January at Washington to 1.5 in May and September. The average seasonal intensity for three hours at noon may be taken as 1.2 gram calories per square centimeter per minute. The total radiation on a horizontal surface, with a clear sky, varies from 0.77 gram calories per minute in December to 1.55 in June. Clouds nearly in line with the sun, but not obscuring it, increase the radiation by about 0.15 gram calories. Otherwise expressed, the maximum radiation that can be received normal to the incident energy is 106 milliwatts per square centimeter.[32] Of the total radiation, only one or two per cent is in the ultraviolet with wave-lengths less than 3889A and more usually may be about half this, while in the case of the quartz mercury arc it may be 30 per cent. Coblentz and Stair [33] found that the upper limit of the total ultraviolet radiation of wave-lengths less than 3100A is less than 0.004 gram calories per square centimeter per minute at sea-level. It cannot exceed 0.3 per cent of the total incident radiation or approximately 300 microwatts per square centimeter. Recently, Coblentz believed this figure should be reduced to less than 100 microwatts per square centimeter.[34] Luckiesh [35] concludes that the best midsummer sunlight supplies not less than 25 microwatts per square centimeter, with a probable value of 40 microwatts per square centimeter, of ultraviolet energy shorter than 3100A.

With the growing appreciation of the rickets-preventing value of the radiations between about 3150 and 2900A, there have appeared a great number of studies of the intensity of the available energy in this region and its seasonal, meteorological, altitudinal and other variations.[36] Especial attention has been

[26] Coblentz, W. W., and Kahler, H., *Sci. Papers Bur. Standards,* No. 378 (1920).
[27] Dorno, C., *Strahlentherapie,* **31,** 341 (1929); Kiepenhauer, K. O., *Naturwiss.,* **25,** 669 (1937).
[28] Cited by Price, W. A., *Ind. Eng. Chem.,* **18,** 679 (1926).
[29] Cited by Forsythe, W. E., and Christison, F., *Gen. Elec. Rev.,* **32,** 664 (1929).
[30] Curve reproduced by Forsythe, W. E., and Christison, F., *Gen. Elec. Rev.,* **32,** 667 (1929).
[31] Coblentz, W. W., and Kahler, H., *Sci. Paper* 378, *U. S. Bureau of Standards,* 1920.
[32] Gordon, N. T., and Benford, F., *Gen. Elec. Rev.,* **33,** 283 (1930).
[33] Coblentz, W. W., and Stair, R., *Bureau Standards J. Res.,* **3,** 629 (1929).
[34] Coblentz, W. W., *Trans. Illum. Eng. Soc.,* **26,** 574 (1931).
[35] Luckiesh, M., "Artificial Sunlight," Van Nostrand, 1920, cited by Coblentz, W. W.; see also Forsythe, W. E., and Christison, F., *J. Opt. Soc. Am.,* **20,** 396 (1930).
[36] Hill, G. L., *Proc. Roy. Soc.,* **102B,** 119 (1927).

devoted to the effects of dust and smoke in lowering the biologically valuable rays.[37] Ashworth[38] considers the effects of winds from towns.

Forsythe and Christison[39] calculated from Abbot's data on the distribution of energy in solar radiations, curves of the transmission of the atmosphere for several wave-length regions, giving the per cents of total radiation and their amounts in milliwatts per square centimeter at Cleveland, Ohio for a horizontal surface, *i.e.*, corrected for the sun's distance from the zenith (Table 17). It must

Table 17.—Transmission of Ultraviolet Rays by Atmosphere.

Region	1 Atmosphere		1.07 Atmosphere June 21		1.5 Atmosphere Feb. 15		2.37 Atmosphere Dec. 21	
	%	Milliwatts	%	Milliwatts	%	Milliwatts	%	Milliwatts
0.31-0.29 μ	0.022	0.024	0.019	0.020	0.0063	0.0061	0.00051	0.0004
Below 0.325	0.24	0.26	0.21	0.22	0.11	0.11	0.029	0.023
Below 0.35	1.1	1.17	1.0	1.07	0.64	0.63	0.27	0.22
Below 0.40	3.9	4.22	3.8	3.97	2.8	2.70	1.62	1.3
0.40-0.76 μ	43.7	46.8	43.9	45.8	42.1	40.4	39.1	31.4
Total		107.0		104.5		96.1		80.2

be noted that these are calculated values, rather than the direct results of actual measurements. The values are in fair agreement with similar calculations by Holladay[40] based upon the assumption that the sun radiates as a black body at 6000°K. The paper of Forsythe and Christison also contains theoretical curves showing the variation of energy below 3250 and below 3100A per square centimeter at Cleveland at various times of day during the winter and summer solstices and the spring and fall equinoxes. There is also given a curve for the

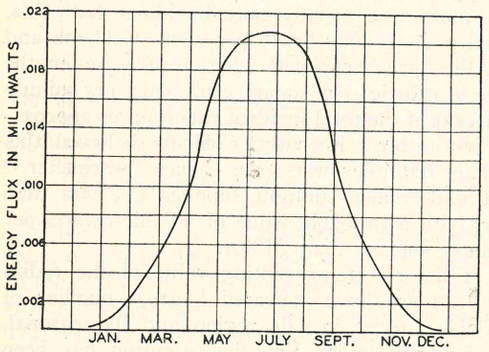


FIGURE 95.

Ultraviolet Energy Below 3100A from the Sun Falling upon a Square Centimeter of the Earth's Surface per Second for the Latitude of Cleveland, Ohio, at Different Times of the Year for 12 Noon. The vertical line above each month denotes its beginning (Forsythe and Christison, *General Electric Review*).

variation of intensity of wave-lengths less than 3100A at noon throughout the year at Cleveland (Figure 95). They concluded it doubtful if any energy in this region is received from the sun in winter at or near a city where the dust and smoke are quite thick. The making of intensity measurements at various wave-

[37] Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assn.*, **89**, 187 (1927).

[38] Ashworth, J. R., *Dept. Sci. Ind. Research, 20th Rept. Investigations of Air Pollution (England)*, 59 (1935); *Chem. Abs.*, **29**, 5560 (1935).

[39] Forsythe, W. F., and Christison, F., *Gen. Elec. Rev.*, **32**, 664 (1929); *J. Opt. Soc. Am.*, **20**, 401 (1930).

[40] Holladay, L. L., *J. Opt. Soc. Am.*, **17**, 329 (1928).

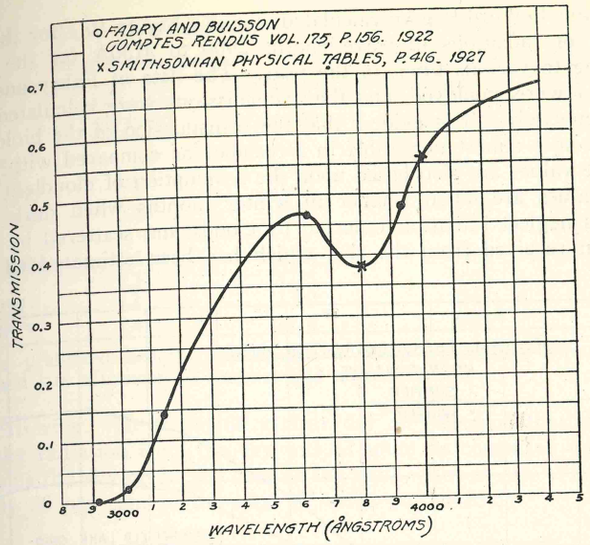


FIGURE 96. Transmission Factors of Earth's Atmosphere (Forsythe and Christison, *General Electric Review*).

lengths in the ultraviolet requires expensive equipment and skill, and comparatively few have made such measurements. In the region around 3000A, the data are of somewhat lower accuracy than in the visible region. There are irregularities when the data of Fabry and Buisson and of Abbot are combined in one curve for the transmission of the atmosphere. (Figure 96.) For this reason more direct determinations are desirable.

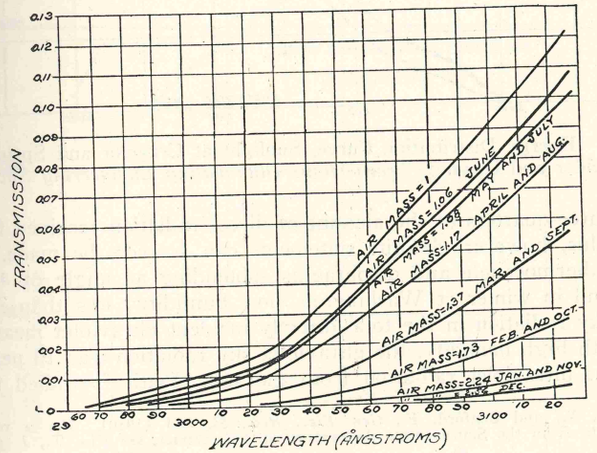


FIGURE 97. Transmission of Atmosphere for Erythema Radiation at Noon, Latitude of Schenectady, N. Y. (Gordon and Benford, *General Electric Review*).

Gordon and Benford [41] give calculated curves (Figure 97) for the atmospheric transmission of radiations of wave-lengths 2900 to 3130A for the "air masses" corresponding to various times of the year. The data of Fabry and Buisson for air mass of 1 were employed, and the transmissions were calculated for the latitude of Schenectady. It is evident that the transmission of the biologically effective rays becomes almost negligible in December as compared with the values of June. These values are also based upon the assumption of cloudless skies, so that the actual values are much smaller in winter months when dark days prevail. These values neglect radiation reflected by clouds and scattered by the blue sky, and radiation received from the sky, which has been estimated to be from one

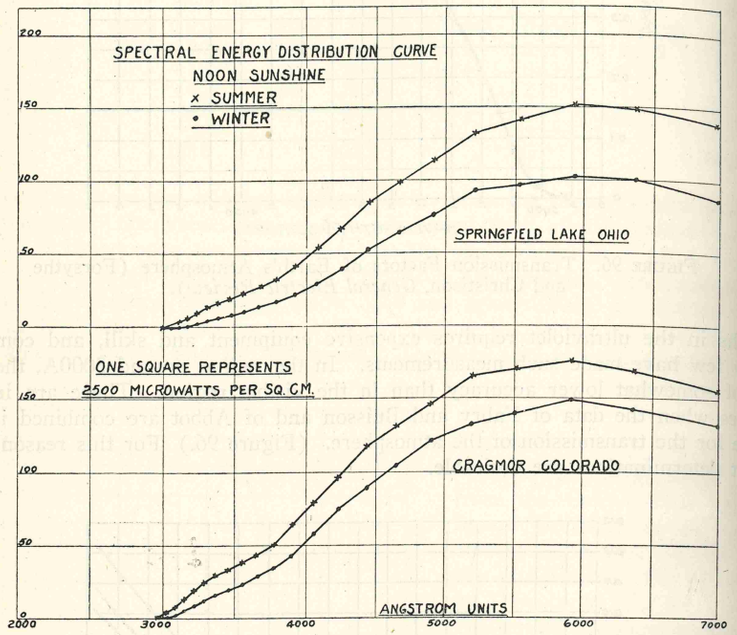


FIGURE 98. Energy Distribution Curve, Sunlight at Cragmor and Springfield Lake. (Greider and Downes, *Transactions Illuminating Engineering Society*).

quarter to three-quarters of the amount of direct radiation received from the sun. Regarding this, however, definite statements can scarcely be made. Coblentz,[42] by using a thermocouple and diaphragms subtending an angle of 45 degrees of the sky, found in winter at Washington (low humidity) less than 7 per cent of ultraviolet sky radiation in the total directly incident ultraviolet measured. On a hazy day with high humidity, the ultraviolet sky radiation was 10 per cent of the total incident ultraviolet radiation from the sun. Pettit [43] studied the effect of

[41] Gordon, N. T., and Benford, F., *Gen. Elec. Rev.*, **33**, 283 (1930). For a recent theoretical treatment of data from the Smithsonian observatory at Montezuma, see Kiu, T., *J. phys. radium*, **9**, 297 (1938).

[42] Coblentz, W. W., *Trans. Illum. Eng. Soc.*, **26**, 576 (1931).

[43] Pettit, E., *Trans. Nat. Tuberculosis Assn. 24th Ann. Meeting*, 110 (1928), cited by Coblentz, W. W.

Table 18.—Transmission of Ultraviolet Rays.

Noon sunshine intensities (watts × 10^{-7} per sq. mm.)

	Antirachitic ultraviolet 2900-3100A	Non-penetrating ultraviolet and visible 3100-6500A	Penetrating red and near infrared 6500-14,000A	Non-penetrating infrared 14,000-120,000A
Springfield Lake, October, 1928	1.2	2894	3660	1760
May-June, 1929	2.3	3404	3786	1834
December, 1929	0.49	2440	3720	1615
Cragmoor, November, 1928	1.6	3534	4432	1860
June, 1929	5.3	4233	4686	2211
January, 1930	1.1	3390	4565	1915
"Clinical sunlight"*	1.4	3214	4045	1810

* This is the preferred heliotherapy dosage in these institutions corresponding to early morning and late afternoon in summer and noon in winter.

atmospheric scattering. He found on a clear day at Pasadena that the intensity of the ultraviolet radiation from the sky was 11 units as compared with 22 units from the sun plus the sky or 50 per cent of the total. But at Mt. Wilson, the sky contributed only 30 per cent of the total (7 units out of 23.3).

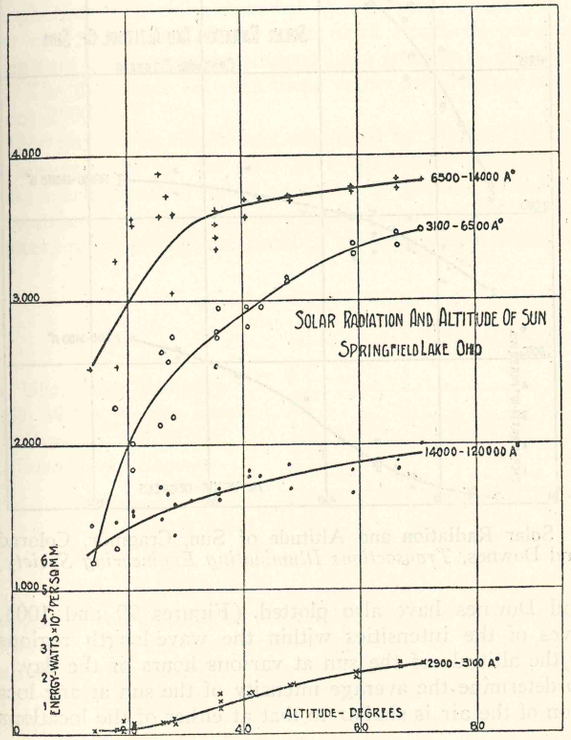


FIGURE 99. Solar Radiation and Altitude of the Sun, Springfield Lake, Ohio. (Greider and Downes, *Transactions Illuminating Engineering Society*).

It is well known that the north sky is richer in ultraviolet than is direct sunlight, but [44] the intensity of light falling in winter at noon on a north window is only about 300 foot-candles as compared with 1100 on a south window.

Greider and Downes [45] reported direct energy measurements at Springfield Lake Sanatorium in Ohio (representative of low altitude locations in this latitude) and at Cragmoor Sanitorium in Colorado ("mountain sun"). Figure 98 shows the noonday values for winter and summer at these locations. The data are summarized in Table 18. Here it is apparent that the variation between summer and winter is less than one to five in the region 2900 to 3100A, which is far less than might be expected from the calculated curves of Gordon and Benford.

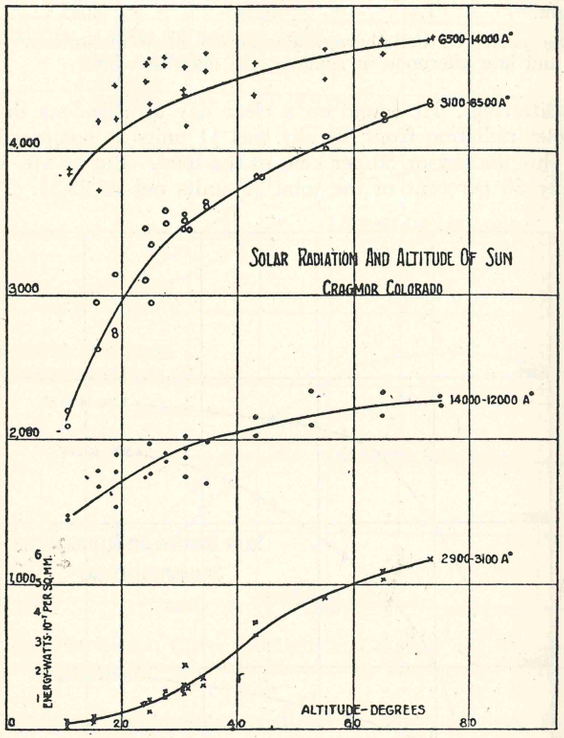


FIGURE 100. Solar Radiation and Altitude of Sun, Cragmor, Colorado. (Greider and Downes, *Transactions Illuminating Engineering Society*).

Greider and Downes have also plotted (Figures 99 and 100), for the two locations, curves of the intensities within the wave-length regions of the table as affected by the altitude of the sun at various hours of the day. These curves can be used to determine the average intensity of the sun at any location at which the transmission of the air is similar to that at either of the locations studied. The

[44] Kimball, H. H., and Hand, I. F., *Monthly Weather Rev.*, **50**, 615 (1922), cited by Coblentz, W. W.

[45] Greider, C. E., and Downes, A. C., *Trans. Illum. Eng. Soc.*, **25**, 378 (1930); **26**, 561 (1931).

altitude of the sun is calculated for the location and time desired and the intensity may then be read from the curves. At the spring and fall equinox the altitude of the sun at noon is 90 degrees minus the latitude. At other times the value is increased or decreased by the amount of the sun's declination. For hours other than noon, the altitude is given by the equation

$$\sin h = \sin \phi \sin \delta + \cos \phi \cos \delta \cos t$$

where h is the altitude of the sun, ϕ its declination, δ the latitude of the place of observation, and t the hour angle, which is approximately 15° for each hour before or after noon.

Such results can of course be only approximations, as they take no account of cloudiness, atmospheric pollution with dust or smoke, or the cleansing effect of rainfall. Coblentz [46] mentions the pronounced effect of dense low-lying strata of finely divided particles from automobile exhausts. The influence of a peak in automobile traffic can be detected in the amount of ultraviolet reaching the earth. Coblentz made photoelectric cell measurements, using a standard screen of barium flint glass. The component of radiation 3130 to 4000A relative to the total ultraviolet 2900 to 4000A measured in June sunlight at sea-level was as follows: direct sunlight, 75 per cent; overcast sky during a light rain (the diaphragmed opening in front of the photoelectric cell subtended 18 degrees), 60 per cent; light overcast sky, 50 per cent; blue sky, 55 per cent; dark cloud, 64 per cent; within the laboratory, 4.5 meters from an open window, light from dark clouds through trees, 64-65 per cent. The difference between these values and 100 per cent is a measure of the component 2900 to 3130A.

The Rentschler ultraviolet meter was employed by Meller, Hibben and Warga in a series of observations on the roof of a nine-story building in Pittsburgh. The cathode was mechanically rotated so as to be normal to the sun's rays. A Westinghouse watthour demand meter recorded the results; each line on the chart of the meter, representing the number of impulses in five minutes, is pro-

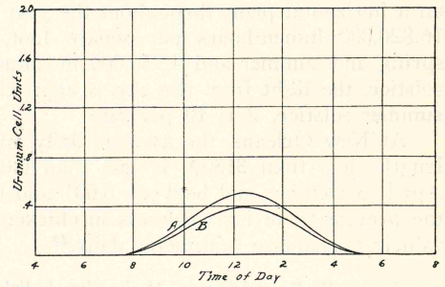


FIGURE 101.

Intensity of Ultraviolet Radiation for December 30, 1930. A. Sun and Sky. B. Sky (Kunerth and Miller, *Transactions Illuminating Engineering Society*).

portional in length to the amount of ultraviolet received at the photo-cell in that period. Records showing the comparative amounts of ultraviolet for an entire day were obtained in this manner. The intermittent obscuring effects of clouds or smoke were readily apparent. Slightly more ultraviolet was recorded on a day having scattered clouds than on a relatively clear day with slightly lower humidity. Even on a clear day there was a 100 per cent change in ultraviolet

[46] Coblentz, W. W., *Trans. Illum. Eng. Soc.*, **26**, 572 (1931).

received in a period of 15 or 20 minutes. For comparison, the zinc sulfide and oxalic acid methods were also employed, but exact comparisons could not be made, as the amounts of sky exposure and the sensitivity curves differed in the methods as employed. Meller and Warga [47] studied the effects of air contaminants on the natural light of cities. Similar data were obtained by Kunerth and Miller [48] using the Rentschler meter without the aid of a graphical recorder at Ames, Iowa. Again the units are arbitrary, merely the number of impulses per second. The curves, Figures 101 and 102, show the ultraviolet in the sun and sky light and in

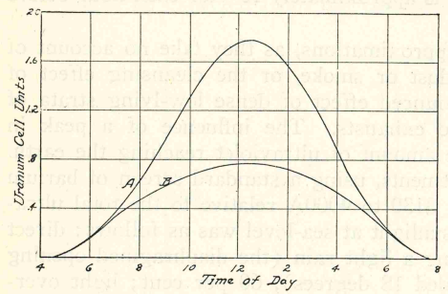


FIGURE 102.

Intensity of Ultraviolet Radiation for June 23, 1931. A. Sun and Sky. B. Sky (Kunerth and Miller, *Transactions Illuminating Engineering Society*).

the latter alone during the course of days in December and June. The energy from the north half of the sky at noon is approximately equal to one-fifth of the total from sun and sky combined. The variation of sky and sun ultraviolet with altitude of the sun and with month of the year are given in tables. The presence of snow on the ground increases the ultraviolet from sun and sky by about 20 per cent. From the data obtained by the meter exposed to sources otherwise calibrated, it appeared that each impulse of the meter was equal to about 39,000 ergs or 3000 ergs per square centimeter. These authors also presented curves for the visible region from the sun and sky and from the latter alone. The total flux on a horizontal plane throughout the year at latitude 42°N if all days are clear is 16,820,000 lumen-hours per square foot, of which 11,870,000 are received in spring and summer and 4,950,000 in autumn and winter. At noon at the winter solstice, the light from the sky is approximately 16 per cent of the total; at the summer solstice, it is 10 per cent.

At New Orleans, the average daily amount of direct solar radiation of wavelengths less than 3130A is less than 0.001 calorie per square centimeter from April to October and between 0.001 and 0.002 during the rest of the year. For the prevention of leg weakness in chickens, the amount required is about 0.00069 calorie per square centimeter daily.[49]

[47] Meller, H. B., and Warga, M. E., *Am. J. Public Health*, **23**, 217 (1933).
[48] Kunerth, W., and Miller, R. D., *Trans. Illum. Eng. Soc.*, **27**, 88 (1932).
[49] Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, **102**, 422 (1932).

Part II

Photochemical Processes